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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LVI NOVEMBER 1961 No. 11

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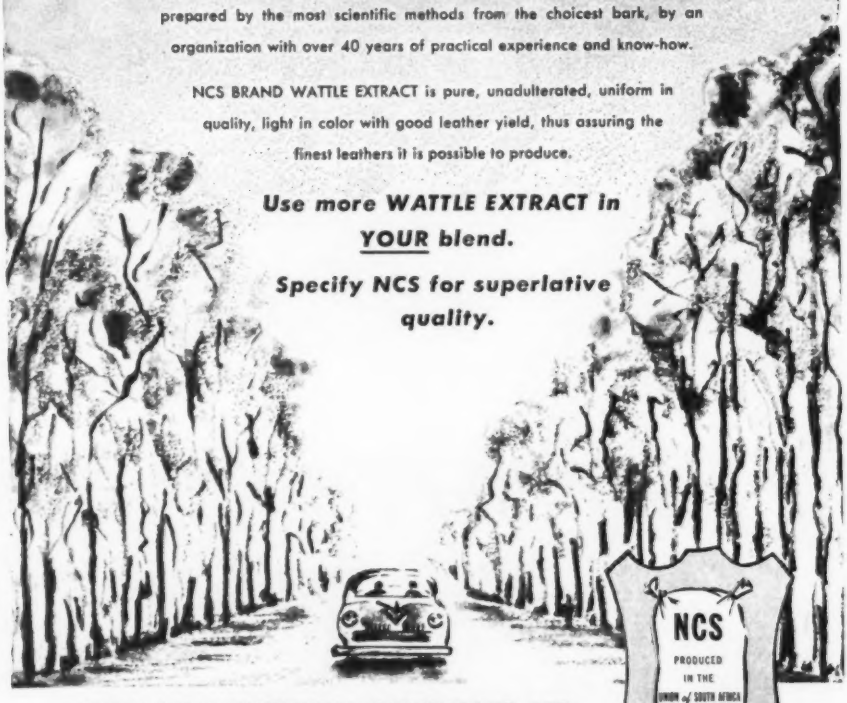

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Vol. LVI NOVEMBER 1961 No. 11

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THE ACTION OF HEAT AND MOISTURE ON LEATHER

PART I. THE STORAGE OF A VARIETY OF COMMERCIAL LEATHERS AT 40°C. AND 100% R.H.*

J. H. Bowes and A. S. Raistrick

British Leather Manufacturers' Research Association
Milton Park, Egham, Surrey, England

ABSTRACT

Studies of the deterioration of leather under warm moist conditions have mainly been concerned with heavy upper leathers of high grease content. In the present work a survey of the behavior of a selection of commercial leathers of various types has been made in order to form a general background to a program of research on the mechanism of the deterioration of leather.

The leathers were stored over water at 40°C. for 6 months, and losses in strength and changes in crackiness, shrinkage temperature, and pH of water extract were determined.

Chrome leathers were the most resistant to the action of heat and moisture and, with the exception of the one sole leather tested, lost little or no strength. Some of the vegetable-tanned leathers also lost relatively little strength but darkened in color and tended to become rather cracky. The resistance of the majority of the semi-chrome and chrome retan leathers was poor, and losses of strength of 80% occurred in some cases. The shrinkage temperature of most of these leathers fell by 10° or more during storage.

The possible causes of the low resistance of these leathers are considered, and their bearing on the behavior of these leathers in wear are discussed.

Limited tests on the same leathers stored over water at 20°C. or in air at 40°C. indicate that little deterioration occurs under these conditions, emphasizing that it is the combined action of heat and moisture which is deleterious.

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INTRODUCTION

The damage to leather which may be caused by the combined action of heat and moisture has long been recognized. The extent to which such

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damage may occur as the result of prolonged exposure to high humidities but relatively low temperatures, however, does not seem to have been fully realized until wartime conditions necessitated the prolonged storage of army footwear under tropical conditions. Work in the last ten to fifteen years has shown that storage under moist conditions at 30°C. or above causes appreciable losses in strength of chrome, vegetable, semichrome, chrome retan, and other combination-tanned leathers (1–10). Increased stiffness, crackiness (2, 9), and fall in shrinkage temperature (5, 7) are also reported. Although mold growth usually occurs when the temperature of storage is 40°–50°C., there is little evidence that this influences the strength or other properties except in so far as it affects the grease (2–6). In some investigations a fall in the pH of water extract of vegetable and retan leathers is reported (4, 5, 11).

Much of this work (4, 5, 7, 9) has been carried out on leathers of high grease content, over 20% in most cases. Changes in the grease have been shown to result in losses of strength (2, 3, 12), and it is, therefore, not certain how far losses in strength are due to such changes in the leather fibers themselves. Also, in the main it has been concerned with heavy-weight vegetable, chrome, semichrome, and more particularly chrome retan leathers prepared for the U.S. Army. Little information on commercial leathers of lower grease contents, other than chrome retan (10, 11), appears to be available. A broad survey of the behavior of a selection of typical commercial sole, insole, upper, and gloving leathers has, therefore, been undertaken in order to form a background to a general research program on the mechanism of the deterioration of leather. In Part II a more detailed examination of the progress of deterioration of vegetable, chrome, semichrome, and chrome retan leathers is described.

EXPERIMENTAL

Notes on leathers examined.—Thirty leathers of various types were collected as indicated in Table I. The leathers classified as semichrome were vegetable-tanned (O, P, and Q, in India) and were retanned with chrome. Those classified as chrome retan, were chrome-tanned first and then given varying degrees of vegetable retannage.

The vegetable-tanned sole leather samples B1–B4 were cut from the same bend and had been treated to reduce water solubles. B1 was untreated; B2, treated with 1% formaldehyde on leather weight; B3, with 1% formaldehyde and 1% urea; and B4, with 0.7% dimethylol urea.

The two vegetable-tanned insoles were from similar tannages consisting of a catechol-pyrogallol blend. The semichrome and chrome retan insoles were from the same firm as the vegetable-tanned insoles, had received a similar vegetable tannage, and were of the same substance. The chrome sole samples F and G were from the same bend before (fore end) and after (tail end) waxing.

TABLE I

ANALYSIS OF LEATHERS

Description of Leathers	Insoluble Ash	Grease	Water Solubles	Fixed Tan	Degree of Tannage	Cr_2O_3 % *moisture and grease free*
	(% *moisture free weight*)					
Vegetable						
A Sole	0.46	5.2	21.1	33.2	82.8	—
B1 Sole	0.64	4.5	23.1	32.5	82.9	—
B2 Sole, formaldehyde-treated	0.58	5.1	6.0	45.6	107	—
B3 Sole, treated with formaldehyde plus urea	0.45	5.1	2.9	44.9	96.1	—
B4 Sole, treated with dimethylol urea	0.37	4.6	2.9	39.9	76.4	—
C Insole, shoulder	0.48	9.2	21.4	29.0	72.7	—
D Insole, butt flesh split	0.26	3.8	8.3	28.3	47.6	—
E Upholstery	0.19	2.5	12.5	33.4	65.0	—
Full Chrome						
F Sole, before waxing	—	1.3	—	—	—	6.89
G Sole, after waxing	—	32.4	—	—	—	6.68
H Side, dyed	—	5.1	—	—	—	5.99
I Side, dyed	—	1.7	—	—	—	5.41
J Side, dyed	—	4.4	—	—	—	4.33
K Side, dyed	—	3.5	—	—	—	4.01
L Calf upper, dyed	—	4.0	—	—	—	6.04
M Cape gloving, dyed	—	6.2	—	—	—	2.85
N Cape gloving	—	10.0	—	—	—	3.26
Semichrome						
O E.I. kip, crust	0.63	8.4	2.6	31.8	57.9	0.76
P E.I. kip, dyed	0.69	9.4	1.5	33.8	66.0	1.52
Q E.I. kip, dyed	1.21	5.3	1.2	27.5	49.2	2.74
R English side	0.66	11.3	0.3	29.3	51.3	1.66
S Insole, shoulder	0.38	8.2	9.9	33.8	74.9	1.12
T Insole, butt flesh split	0.59	5.5	2.4	32.2	56.2	0.74
Chrome Retan						
U Sole	0.82	4.7	23.1	28.4	69.1	0.78
V Side	0.82	5.0	1.1	7.1	9.7	5.44
W Insole, shoulder	0.74	6.4	4.9	33.0	58.3	2.81
X Cape gloving	7.30	10.4	3.7	9.7	15.3	2.61
Miscellaneous						
α Zirconium, hide, grain split	—	—	—	—	—	—
β Chamois	—	—	—	—	—	—
γ Chamois, rot-resistant	—	—	—	—	—	—

The two gloving leathers N and X were from the same tannage, but X had been given a further treatment with 25% liquid vegetable tanning extract based on mimosa and 2–3% syntan on dry weight. M had been lightly dyed with neolan and wood dye.

Of the two chamois leathers, γ had been classified as rot-resistant by a rapid incubation test (13). Neither contained any detectable formaldehyde.

Sampling and storage.—Samples were cut from the britch areas of most leathers (A, D, G–L, O, P, R, T, U, and V), from the fore end of the butt of F, and from the center of the half shoulders, D, S, and W, about 4″ from the backbone. With the small skins, samples were taken from each side, avoiding the backbone. The location of samples E, Q, and α was not known.

For the examination of the effect of storage over water at 40°C. samples were all cut from an area 12″ x 8″ in such a way that each test sample could be paired with a corresponding control sample adjacent to it, so that the actual tests on control and deteriorated leathers were made as near to each other as possible.

The test samples were suspended over water in glass tanks 5″ x 7″ covered with a glass plate and stored in an incubator at 40°C. for 6 months. A small beaker containing toluene was placed in each tank to discourage mold growth. The corresponding control samples were stored in polyethylene bags in the laboratory at temperature 18°–22°C. Both sets of samples were then tested together, and the percentage loss in strength for each pair was calculated.

Further samples of some of the leathers were stored for 6 months over water at 20°C. or hanging freely in an incubator at 40°C. In this case only six samples 6″ x 1½″ for buckle tear tests were included, measurements being made on the same samples before and after storage.

After removal from the tanks the leathers were air-dried.

Examination of leathers.

Analyses.—The analysis of the original leathers was carried out by the official S.L.T.C. methods (14). Chrome was determined by perchloric acid oxidation. Fixed tan in the combination-tanned leathers was calculated by difference using a factor of 2.5 × Cr_2O_3 for "chrome tan". For pH of water extract 2.5 g. leather, either ground or in small pieces 2 mm. sq., were extracted with 50 ml. water for 24 hours at room temperature with occasional shaking (A.L.C.A. Official Method D35). The analyses are recorded in Table I.

Physical tests.—The leathers were conditioned at 21°C. and 70% R.H. Buckle tear loads on samples 4″ x 1.5″ and tensile strength (breaking load) were determined as described in S.L.T.C. Official Methods (14). Percentage losses in strength for each pair of samples were calculated. With most leathers there was reasonable agreement between replicates, but only differences of ten or more in the figures for percentage loss can be considered real.

RESULTS

In spite of the presence of toluene mold, developed on some of the leathers stored over water at 40°C.; on the vegetable-tanned leathers B1, B2, B3,

TABLE II

SOME EFFECTS OF MOIST STORAGE AT 40°C.

Leather and Tannage	Water Uptake during Storage	Mold Growth*	Crackiness after Storage*	pH of Water Extract		Shrinkage Temperature °C.	
				Control	Stored	Control	Stored
Vegetable							
A	13	++	++	3.61	3.48	77	81
B1	29	++++	+	3.68	3.49	78	87
B2	15	++++	++	3.48	3.18	93	96
B3	21	++++	++	3.46	4.16	96	98
B4	32	++++	+++	3.50	5.43	94	98
C	11	++++	+	3.58	3.19	74	82
D	23	0	+	4.43	4.10	77	84
E	34	++++	+	3.44	3.34	71	82
Full Chrome							
F	38	0	++	3.65	3.46	112	114
G	31	0	++	3.57	3.52	110	114
H	28	0	0	3.52	3.32	115	117
I	35	0	0	3.08	2.95	110	115
J	39	0	0	3.03	2.96	101	109
K	45	+	0	3.24	3.24	112	114
L	22	0	0	3.68	3.95	110	115
M	170‡	+	0	4.35	4.48	98	100
N	77‡	0	0	4.85	4.74	102	104
Semichrome							
O	19	+	++	2.98	3.09	89	78
P	21	0	+	3.35	3.28	99	76
Q	36	++	+	3.52	2.99	119†	97†
R	25	0	+++	3.14	3.03	98	83
S	40	0	+++	2.68	2.68	78	77
T	19	++	+	3.08	2.84	89	73
Chrome Retan							
U	22	++	++	3.73	3.35	81	86
V	32	0	+	3.28	3.24	114†	112†
W	18	0	++	3.15	2.93	112†	100†
X	41	++	0	4.46	4.15	99	96
Miscellaneous							
α	57	++	—	3.84	3.56	84	85
β	151‡	0	—	—	—	64	63
γ	44	0	—	—	—	73	71

* +very slight; ++ slight; +++ medium; ++++ extensive
† Shrinkage temperatures of all chrome leathers and those indicated by †, determined in 75% glycerol/water.
‡ Leather stretched during storage and may have touched water surface.

B4, C, and E and on the retan leather U after one month, and on a number of others at a later stage. The extent of this mold growth at the end of the six-month storage is indicated in Table II.

The uptake of water during storage was determined, as it was thought that this might influence deterioration. No correlation with loss of strength or other changes could be detected, however.

TABLE III

THE EFFECT OF STORAGE OVER WATER AT 40°C. ON STRENGTH

Leather and Tannage	Buckle Tear Load		Tensile Strength Breaking Load	
	Control lb.	% Strength Retained after Storage	Control lb.	% Strength Retained after Storage
Vegetable				
A	487	51	455	50
B1	408	89	476	70
B2	260	87	356	71
B3	291	83	335	57
B4	317	89	277	77
C	150	91	270	66
D	162	80	355	65
E	69	85	225	44
Full Chrome				
F	318	46	315	67
G	319	49	432	63
H	56	108	97	105
I	93	117	233	105
J	59	100	137	77
K	52	116	106	100
L	12	102	42	110
M	58	83	—	—
N	13	114	—	—
Semichrome				
O	59	53	157	46
P	81	56	230	54
Q	41	52	106	35
R	43	35	92	28
S	191	32	276	17
T	92	31	151	35
Chrome Retan				
U	391	66	437	59
V	66	83	104	64
W	42	23	68	21
X	11	60	—	—
Miscellaneous				
α	31	93	95	87
β	11	19	—	—
γ	8	87	—	—

The chrome leathers were the least affected by the warm moist storage. There was little change in their appearance, and with the exception of the sole leather, they lost little or no strength. (*See Table III.*) The leathers tended to become rather stiffer, but only the sole leather, both waxed and unwaxed, showed signs of crackiness. Contrary to the observations of some workers (7) the shrinkage temperature of most of the chrome leathers increased by 2°–10°C. (*See Table II*).

The vegetable-tanned leathers darkened in color and all developed some degree of crackiness, but with the exception of leather A, losses in buckle tear load were less than 20%. Losses in tensile strength were rather greater but still relatively small compared with that of most of the vegetable-chrome combination leathers. After determination of the shrinkage temperature the leather samples were somewhat gelatinous in appearance and texture, suggesting that there had been some loss of cohesion during the storage which,

TABLE IV

THE EFFECT OF STORAGE OVER WATER AT 20°C. OR IN AIR AT 40°C.

Leather and Tannage	% Strength (Buckle Tear Load) Retained after Storage		Shrinkage Temperature °C.	
	20°C. over water	40°C. in air	20°C. over water	40°C. in air
Vegetable				
A	101	108	74	74
C	106	103	73	73
E	104	105	68	67
Chrome				
F	106	101	114	109
G	120	89	110	107
H	106	107	116	109
I	126	100	111	105
J	120	107	105	88
L	125	113	109	98
N	99	102	95	90
Semichrome				
O	89	95	85	82
P	97	97	95	92
R	98	78	91	88
T	99	95	85	84
Chrome Retan				
U	99	95	84	80
V	98	84	111	105
W	90	84	103	102
X	90	90	90	91
Miscellaneous				
α	110	98	84	63
β	102	83	64	59
γ	110	—	70	—

on heating, allows some disorganization of the collagen structure. The apparent increase in shrinkage temperature on storage is probably due to this, stretching of the sample masking the initial stages of the fiber shrinkage.

The resistance of the semichrome and retan leathers was almost uniformly poor; they became darker in color, the strength of many was reduced by 50% or more, and a few became very cracky on the grain, e.g., R and S. The only leathers which retained a reasonable proportion of their strength were the lightly retanned side of high chrome content (V) and to a lesser extent the sole leather which contained little chrome and was not very different from a vegetable-tanned leather.

Of the miscellaneous leather, the zirconium behaved similarly to the chrome-tanned upper leathers. The oiled, tanned leather γ, classified as rot-resistant, was almost unaffected by storage, but the other was harsh in appearance and feel and became very weak. The greater resistance of leather γ is probably associated with its higher shrinkage temperature, indicating that cross links may have been formed from aldehydes produced by oxidation of the oil.

The limited tests carried out on the effect of storage over water at 20°C. or in the air at 40°C. indicate that under these conditions there is little loss of strength or general deterioration. (*See Table IV.*)

Apart from some darkening of the leathers containing vegetable tan, moist storage at 20°C. had no obvious adverse effects, and the strength of the vegetable and chrome leathers was, in fact, slightly increased. Dry storage at 40°C. also caused small increases in the strength of the vegetable and chrome leathers, but there were slight decreases with the semichrome and chrome retan leathers. The strength of the waxed chrome sole also decreased, probably because of changes in the grease. This leather, and also the unwaxed chrome sole, became cracky, and the vegetable and retan soles rather cracky, but the other leathers were apparently unaffected.

The shrinkage temperature of the combination-tanned leathers was decreased by 5°–10°C. by storage under both conditions, and that of the chrome and zirconium leathers by about 10°C. by dry storage at 40°C. The shrinkage temperature of the other leathers was unaffected.

DISCUSSION

It is clear from these results that it is the combined action of heat and moisture which is deleterious to leather rather than either heat or moisture alone, and that the type of tannage, vegetable, chrome, or combination of vegetable and chrome, is one of the most important factors governing stability. It may be deduced that chrome leather is likely to be the most resistant, and that vegetable-tanned leathers of relatively good resistance can also be produced, but that semichrome leathers, as well as chrome retan leathers, are likely to deteriorate badly under such conditions.

The stability of the majority of chrome-tanned leathers tested does not ubstantiate earlier work (5, 7, 9), in which appreciable losses in strength were found under comparable conditions. In most cases, however, these losses in strength were observed with leathers of high grease content, or with sole or heavy army upper leathers similar to the chrome sole in the present investigation. The poorer resistance of such heavy-substance leathers remains unexplained; in the present work it was not associated with any difference in pH or in chrome content or distribution.

Variations in stability of any one type of leather could not be directly related either to pH or to the composition of the leather. The relatively high stability of the lightly retanned leather V is probably due to its high chrome content, and the loss of strength of the chrome gloving M may be associated with the use of a vegetable mordant.

The poor stability of chrome retan leathers has been observed by Sykes and Williams-Wynn (10, 11, 15), both under normal and accelerated conditions of aging. As in the present investigation they found a fall in pH of water extract, which was later followed by an increase which they attributed to hydrolytic breakdown of the collagen. It is generally agreed that during retannage with vegetable tans sulfate or other anions are displaced from the chrome complex, and Amos, Thompson, and Tolliday (17) have shown that this displacement continues when the leather is stored wet. As suggested by Sykes and Williams-Wynn (10) such displacement probably accounts for the fall in pH of chrome retan leathers on storage, Chrome is also displaced during retannage (17), and it seems likely that carboxyl groups of the protein are also slowly displaced from the chrome complex during storage, leading to detannage. Such a mechanism would account for the large falls in shrinkage temperature which occurred during storage.

Although the semichrome and retan leathers are more affected by moist heat than chrome- or vegetable-tanned leathers, it does not necessarily follow that this will also be true in wear. Experiments have shown that the presence of vegetable tannins reduces the amounts of chrome which can be extracted from leathers by lactate solutions (18); hence such leathers may be more resistant to the detanning action of perspiration than full chrome leathers. Also, since perspiration tends to increase the pH of the leather, thus increasing oxidation of tan and displacement of chrome (19), the slow production of acidity by the combination-tanned leather may be beneficial rather than deleterious in wear.

REFERENCES

1. Kanagy, J. R., and Tobias, P. E. *JALCA*, **37**, 426 (1942).
2. ———, Charles, A. M., Abrams, E., and Tener, R. F. *JALCA*, **41**, 198 (1946).
3. ———, Seebold, R. E., Charles, A. M., and Cassel, J. M. *JALCA*, **44**, 270 (1949).
4. Lollar, R. M. *JALCA*, **49**, 605 (1954).

5. Roddy, W. T., and Jansing, J. J. *JALCA*, **49**, 773 (1954).
6. Mitton, R. G., and Turner, J. M. *J. Soc. Leather Trades Chemists*, **39**, 343 (1955).
7. Mann, G. W., and Steiner, E. T., as quoted by Seligsberger, L., and Mann, G. W., in *Chemistry and Technology of Leather Manufacture*, Vol. II (New York: Rheinhold, 1958) 489.
8. Seligsberger, L., Mann, G. W., and Clayton, H. *JALCA*, **53**, 627 (1958).
9. Mitton, R. G., and Wyatt, K. E. Unpublished.
10. Sykes, R. L., and Williams-Wynn, D. A. *J. Soc. Leather Trades Chemists*, **45**, 214 (1961).
11. ——— — ———. *Ibid.*, **43**, 265 (1959).
12. Mitton, R. G. Unpublished.
13. Green, G. H. Unpublished.
14. Official Methods of Analysis. *Soc. Leather Trades Chemists*. 1957.
15. Sykes, R. L. and Williams-Wynn, D. A. *J. Soc. Leather Trades Chemists*, **45**, 16 (1961).
16. Amos, G. L., Thompson, G. W. H., and Tolliday, J. D. *Ibid.*, **42**, 342 (1958).
17. Gustavson, K. H. *The Chemistry of Tanning Processes*, (New York: Academic Press, 1956) Chap. 9.
18. Moss, J. A. In preparation.
19. Bowes, J. H., and Moss, J. A. *J. Soc. Leather Trades Chemists*, **44**, 419 (1960).

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Salt was early known as a preservative and was certainly used for the curing of hides and skins, but the first mineral tannage (German "Weisz-gerberei") was undoubtedly the alum process, which we will find in use in the Ancient Near East at an early date. The process was formerly known as "tawing"; it was carried out by the whitetawyers. The skins were soaked in a strong solution of alum and common salt in the proportion of two to one. Such tawed leather is snowwhite and rather stiff. It can be softened by working over a curved blunt edge as depicted in Egyptian tomb paintings. This leather may be rather stretchy but it is not at all resistant to water and has to be dry-cleaned (gloves!) A slightly modified process of tawing uses in addition to alum and salt, egg yolk and flour. This mixture was trodden in with bare feet. Tawed objects have been found in prehistoric Egyptian tombs and there is clear evidence of its use in the Semitic world and India at an early date.

In eighth century Spain, some time after the Moorish conquest, the manufacture of "cordwain" leather started at Cordova. This leather soon became famous all over Europe. The original cordwain leather was made from the skin of the mouflon (*Ovis musimon*), the haired sheep of Corsica and Sardinia. Soon, however, there were several kinds of Spanish leather involving amongst others tanning with sumach and tawing with alum. One type was silvered or gilded and embossed, but a brilliant scarlet is believed to have been obtained by tawing with alum and tin salts and then dyeing with kermes. From Spain the mineral tanning process was passed on to Western Europe during the ninth century. —R. J. Forbes. "Leather in Antiquity" in *Studies in Ancient Technology*, Vol. V (Leiden, the Netherlands: E. J. Brill, 1957).

THE ACTION OF HEAT AND MOISTURE ON LEATHER

PART II. THE STORAGE OF VEGETABLE, CHROME, SEMICHROME, AND CHROME RETAN LEATHERS AT 40°C. AND 60°C. AND 100% R.H. FOR VARYING PERIODS OF TIME*

A. S. RAISTRICK

British Leather Manufacturers' Research Association, Milton Park, Egham, Surrey, England

ABSTRACT

In Part I of this series the effect of storage at 40°C. over water on a wide range of commercial leathers was reported. To examine the effect of variations in the conditions and time of storage, and the chemical changes occurring, four leathers, chrome-tanned, vegetable-tanned, semichrome, and chrome retan, were stored in closed jars over water for periods of up to 72 weeks at 40°C. or 15 weeks at 60°C. and tested at intervals for buckle tear load, shrinkage temperature, pH of water extract, and solubilization of protein.

All the leathers lost about 50% of their strength after 5 weeks at 60°C. over water. The three leathers containing vegetable tan lost their fiber structure after 10 to 15 weeks and were very dark in color. The chrome leather, although weak, had changed little in appearance. At 40°C. the chrome- and vegetable-tanned leathers were relatively unaffected, but the combination-tanned leathers lost over 80% of their strength in 72 weeks.

Mold growth caused considerable losses in strength in the chrome-tanned leather, but the other three leathers were not adversely affected.

The shrinkage temperature of the chrome- and vegetable-tanned leathers increased with extended time of storage, but that of the combination-tanned leathers decreased. Changes in the pH of water extract of the leathers were small until the leathers lost their fiber structure, when increases from about pH 3 or 4 to pH 5 or 6 were observed in some cases.

Only small increases in nitrogen soluble in 0.1*N* sodium bicarbonate were found. The nitrogen soluble in 5*M* acetic acid increased

*This work was started while the author was British Leather Manufacturers' Research Association Research Fellow in the Department of Leather Industries, Leeds University, and is now incorporated in a research program sponsored by the United States Department of Agriculture under the authority of U. S. Public Law 480.

slowly as the leathers lost strength and then more rapidly when the fiber structure began to be lost. Although the chrome-tanned leather became very weak in some instances, its soluble nitrogen was always low. In the grossly deteriorated leathers containing vegetable tan the volatile nitrogen in the extracts was very high, indicating that deamination of the amino acids of the collagen had occurred.

The extractability of the chrome tan was reduced by storage, suggesting that considerable changes had occurred in the chrome complex.

The mechanism of deterioration is discussed.

INTRODUCTION

In Part I (1) of this series the resistance of a wide range of leathers to storage at 40°C. over water was examined. Previous workers (2–10) have reported that these conditions cause loss in strength, increased stiffness, crackiness (3, 10), and fall in shrinkage temperature (6, 8). Where the results given in Part I could be compared with this earlier work, good general agreement was found, except that unexpected increases in the shrinkage temperatures of chrome leathers were found.

Such chemical analyses as have been made on deteriorated leathers (2, 3, 5, 6, 11) have been restricted to the official methods of analysis and the measurement of carbonate- or bicarbonate-soluble nitrogen. In particular it should be mentioned that increases in soluble nitrogen were very small and could not be related to the losses in strength (3, 5).

The present investigation was undertaken to examine more fully the progressive deterioration of a small group of leathers under a rather wider range of conditions. Two temperatures of storage were chosen: 40°C., as being representative of the more severe conditions which may be encountered in wear, and 60°C., to determine whether the accelerated deterioration occurring at this higher temperature follows the same pattern as that at 40°C.

EXPERIMENTAL

Description of leathers.—Four leathers, chrome-tanned, vegetable-tanned, semichrome, and chrome retan, were used in this investigation. They were prepared commercially from English oxhides which had been given a mellow liming and had been bated. The two butts for chrome tanning were pickled in 5% sodium chloride and hydrochloric acid to pH 3.5 and tanned with a 33% basic glucose-reduced chrome sulfate liquor, 4% Cr_2O_3 on limed

weight being offered. They were basicified to pH 4.0 with sodium bicarbonate. Following tanning they were given a short wash, but they were not neutralized. The butt for retanning was drummed in a 70° Bk. vegetable tan liquor (*see below*), tan being added until penetration was almost complete.

The butts for vegetable and semichrome tannage were tanned on the countercurrent system with a blend of lightly sulfited quebracho containing 10% chestnut. The barkometer of the final liquor was about 70°.

The vegetable-tanned butt was given a very short wash. The butt for semichrome leather was washed well and then drummed with the chrome liquor described above, 2% Cr_2O_3 on limed weight being offered.

The leathers were then air-sammed, lightly oiled with neatsfoot oil, nailed on frames, and dried at atmospheric temperature. The analyses of the leathers are given in Table I. The chrome leather had a higher grease content than intended, presumably because the original hide had a high natural fat content.

TABLE I

ANALYSIS OF LEATHERS BEFORE STORAGE

(*Grams/100 grams air-dry leather*)

	Chrome	Vegetable	Semichrome	Chrome Retan
Moisture	15.6	12.4	14.6	12.5
Grease	8.3	2.9	3.2	3.7
Water solubles	5.6	17.6	3.3	8.3
Insoluble ash	4.3	0.2	2.8	1.8
Hide substance	63.7	43.9	52.8	51.4
Cr_2O_3	3.9	—	2.4	1.8
Fixed tans*	—	23.0	20.0	19.7
Degree of tannage	—	52	38	38
pH of water extract	3.9	4.2	3.3	3.2

*Fixed tans were determined by difference using a factor of 2.5 × Cr_2O_3 for "chrome tan" in the combination-tanned leathers.

Method of storage.—The leathers were stored at approximately 100% R.H. at 60°C. for 2, 5, 10, or 15 weeks and at 40°C. for 12, 36, and 72 weeks. They were hung from glass rods over water in closed jars, which were then placed in incubators at the appropriate temperatures. Duplicate sets were stored at 40°C. with a small beaker of toluene in the bottom of the jar to discourage mold growth. This was effective provided the slow loss of toluene by evaporation was made good when necessary. The control samples were stored in the laboratory (18°–22°C.).

Sampling.—Buckle tear rather than tensile strength determinations were used to assess losses in strength, since the samples required are smaller

and more compact. A preliminary test indicated that eight samples for each period of storage would give an adequate estimate of the changes in strength.

The pieces of leather were cut as indicated in Fig. 1. The butt was divided into sixteen blocks of nine pieces cut symmetrically with respect to the backbone. Pieces from each pair of symmetrically placed blocks were then allotted at random to the treatments in such a way that each experimental piece could be compared with a corresponding control piece cut from the opposite side of the backbone.

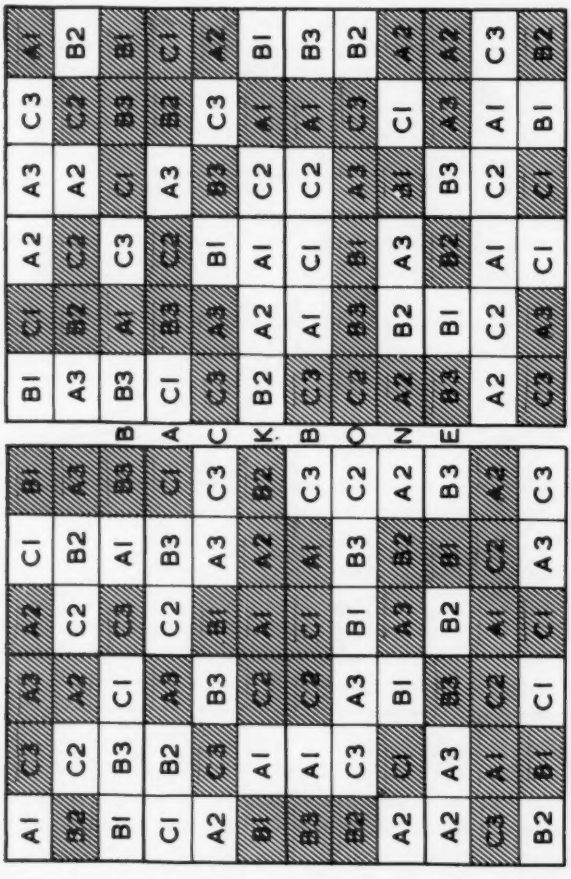
B1 C1 A2 A3 C3 A1
A3 B2 C2 A2 C2 B2
B3 A1 C3 C1 B3 B1
C1 B3 C2 A3 B2 C1
C3 A3 B1 B3 C3 A2
B2 A2 A1 C2 A1 B1
C3 A1 C1 C2 A1 B3
C2 B3 B1 A3 C3 B2
A2 B2 A3 B1 C1 A2
B3 B1 B2 B3 A3 A2
A2 C2 A1 C1 C3
C3 A3 C1 B1 B2
B A C K. B O N E
A1 C3 A3 A2 C1 B1
B2 C2 C2 B2 B2 A3
B1 B3 C1 C3 A1 B3
C1 B2 A3 C2 B3 C1
A2 C3 B3 B1 A3 C3
B1 A1 C2 A1 A2 B2
B3 A1 C2 C1 A1 C3
B2 C3 A3 B1 B3 C2
A2 C1 B1 A3 B2 A2
A2 A3 B3 B2 B1 B3
C3 A1 C2 A1 C2 A2
B2 B1 C1 C1 A3 C3
EXPERIMENTAL PIECE.
CONTROL PIECE.
A - 60°C. OVER WATER
B - 40°C. OVER WATER
C - 40°C. OVER WATER PLUS TOLUENE
1 - SHORTEST TIME OF STORAGE
2 - SECOND " "
3 - LONGEST " "

FIGURE 1.—Typical sample-cutting plan. Each experimental piece is paired with a control piece cut symmetrically from the opposite side of the backbone.

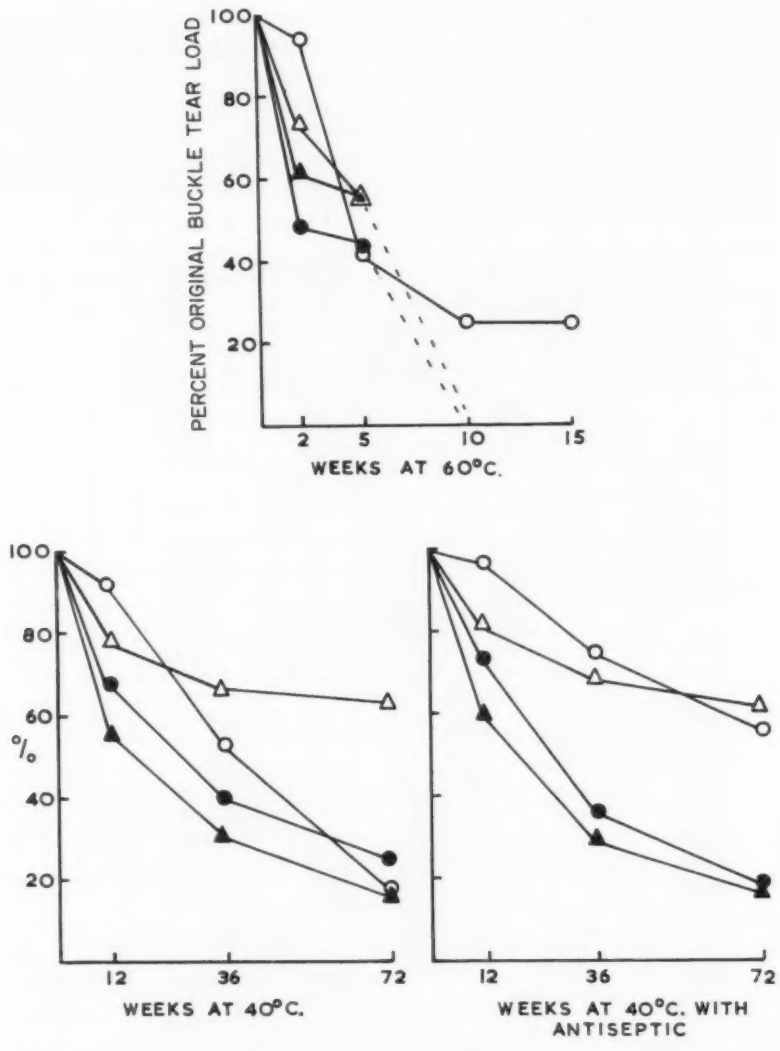

FIGURE 2.—Percentage of original buckle tear load remaining after storage.

△ ——— △ Vegetable-tanned
○ ——— ○ Chrome-tanned
▲ ——— ▲ Semichrome
● ——— ● Chrome retan

Buckle tear load.—The buckle tear load was determined by the S.L.T.C. official method (12) except that the pieces were 3½" x 1½". Each control piece was tested at the same time as its experimental partner.

Shrinkage temperature.—The determinations on the vegetable-tanned leather were made in water, and on the other three leathers in 75% v/v glycerol/water. All samples were thoroughly wet back with water before testing. The results are the mean of at least three determinations.

Analysis of leather.—The leathers were cut into about 3-mm. squares, or if too brittle to cut, they were ground to pass a 20-mesh sieve.

Analyses were then carried out as described in Part I.

Extractions with 0.1*N* $NaHCO_3$, 2*M* $CaCl_2$, and 0.1*M* acetic acid were made using a 1:10 w/v ratio of leather to solution for 48 hours at room temperature with occasional shaking. Extractions with the same ratio of 5*M* acetic acid were for 7 days at room temperature, as it was found that the extraction was slower than in the other solutions.

The total nitrogen in the extracts was determined by a standard micro-Kjeldahl procedure (13) and the volatile nitrogen by direct distillation from borate buffer at pH 11, after neutralization with sodium hydroxide where necessary.

With the chrome, semichrome, and chrome retan leathers the chrome content of the 5*M* acetic acid extracts was determined by the perchloric acid oxidation method.

RESULTS

Appearance and loss in strength.—After only two weeks' storage over water at 60°C. all the leathers containing vegetable tan had darkened in color. The semichrome and chrome retan leathers had lost 40% to 50% of their original strength and the vegetable-tanned leather 26%, but the chrome leather was unaffected.

After five weeks, however, the difference between the leathers was less, since further losses in strength of the semichrome and chrome retan leathers were small, while that of the chrome leather was considerable.

On further storage the vegetable-tanned leather deteriorated rapidly; after ten weeks it had lost its fiber structure and was dripping as a very dark viscous fluid on the bottom of the jar. It was, therefore, removed from storage. The chrome leather at this stage retained only 25% of its original strength.

After a further five-week storage the combination-tanned leathers had also lost their fiber structure, were very dark in color, and had become toffee-like in consistency. The chrome leather showed little change in color or appearance. The grain was rather cracky, but otherwise it looked to be a

satisfactory piece of leather. Its strength had not been reduced in the last five weeks of storage and remained at 25% of its original value.

Toluene effectively prevented mold growth on the leathers stored at 40°C. In the absence of toluene the three leathers containing vegetable tan rapidly developed a profuse mold growth. The chrome leather remained free of mold for about 12 weeks, and growth was never as extensive as on the other leathers. This leather, however, was the only one whose behavior was appreciably affected by the mold growth (*see Fig. 2*). Losses in strength of the vegetable, semichrome, and chrome retan leathers were similar under both conditions of storage at 40°C., but with the chrome leather losses were much greater in the presence of mold.

The vegetable-tanned leather was much more resistant to storage at 40°C. over water than at 60°C. over water, and after 72 weeks it had only lost about 30% of its strength. It was slightly darker in color than at the start of storage, but otherwise its appearance was still quite good. The semichrome and chrome retan leathers were by far the most adversely affected. After 72 weeks they had lost about 80% of their strength and were beginning to show the plastic flow and loss of fiber structure found after 15 weeks at 60°C.

A microscopical examination of the fiber structure of the leathers confirmed the conclusion drawn from their macroscopic appearance. In the case of the chrome leather stored at 60°C. over water, however, although the fiber structure was still quite good, the fibers had a slightly glassy appearance, and the structure was rather more open than in the control samples.

Shrinkage temperature.—The shrinkage temperature of the chrome leather increased during storage, except when there was mold growth on the leather. The shrinkage temperature of the vegetable-tanned leather also tended to increase. Measurements made on the few pieces which still retained some fiber structure after 10 weeks at 60°C. still indicated a shrinkage temperature of 80°C. The shrinkage temperatures of the combination-tanned leathers decreased steadily as storage proceeded.

pH of water extract.—There was little change in pH of water extract as a result of storage at 60°C. over water. With the vegetable-tanned leather there was a slight decrease in pH, and with the chrome leather there was a slight increase. With the combination-tanned leathers a slight decrease was followed by an increase to values above the initial pH. A similar observation was made by Sykes and Williams-Wynn on accelerated aging tests on chrome retan leathers (11).

At 40°C. in the absence of mold there were small decreases in pH of both chrome- and vegetable-tanned leathers. As at 60°C. the pH of both the semichrome and retan leathers decreased at first, and then increased, but in this case the pH of the retan leather rose above 5.0.

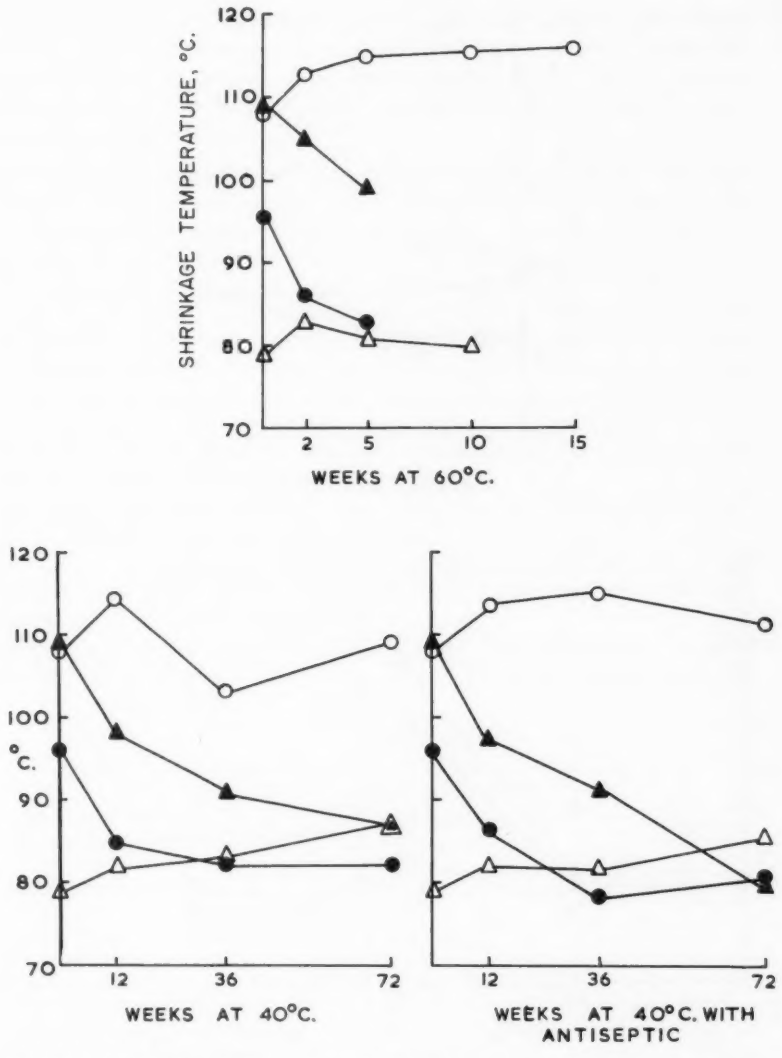

FIGURE 3.—Shrinkage temperatures of leathers after storage. Vegetable-tanned leather measured in water, others in 25% aqueous glycerol.

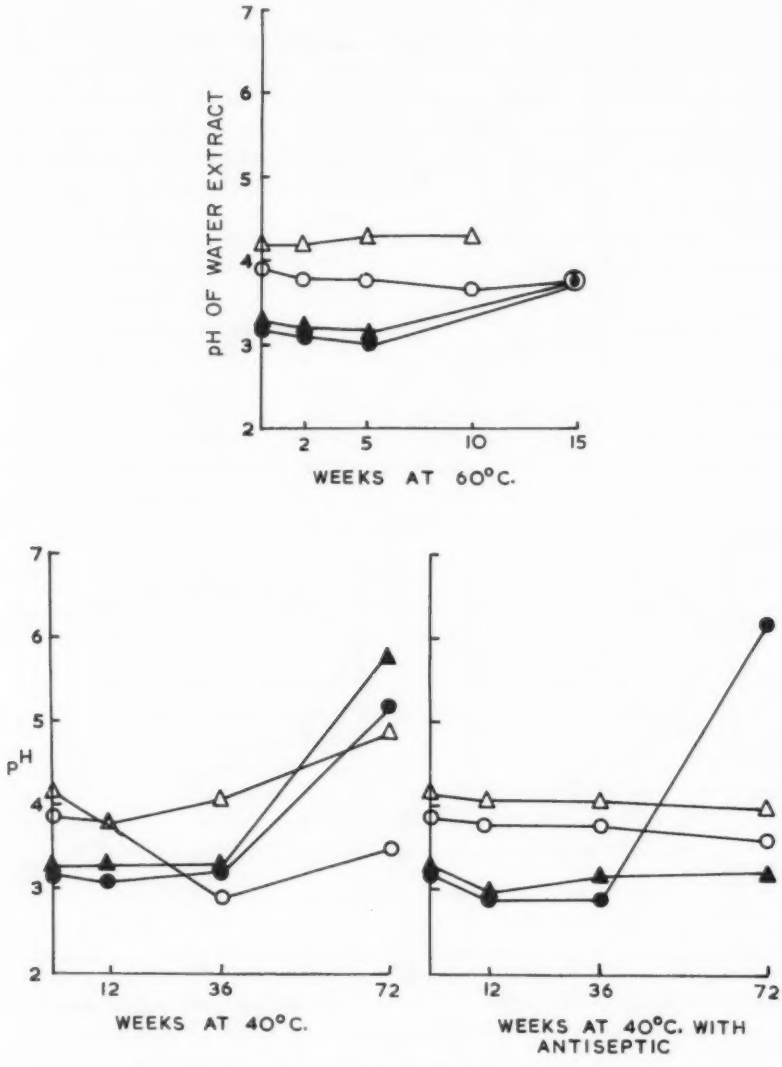

FIGURE 4.—pH of water extract of leathers after storage.

△——△ Vegetable-tanned
○——○ Chrome-tanned
▲——▲ Semichrome
●——● Chrome retan

When mold growth occurred, the pH changes were greater. The vegetable-tanned leather showed a decrease followed by an increase, as did the combination-tanned leathers. The chrome-tanned leather was relatively unaffected after 12 weeks, but further storage produced a large decrease followed by a small increase.

Extraction of degraded protein.—The breakdown of protein in leather has usually been followed by extraction with mildly alkaline solutions and determination of the dissolved protein as nitrogen. The results so obtained have generally shown little correlation with strength changes (3, 5).

In a preliminary examination samples of the vegetable- and chrome-tanned leathers stored at 60°C. over water for the longest time were extracted with 0.1*N* $NaHCO_3$. The leather was filtered off, and the nitrogen was determined on the extract (*see Table II*). The soluble nitrogen of the deteriorated leathers was only slightly greater than that of the controls. The vegetable-tanned leather had lost its fiber structure completely during storage, and it was evident that these small increases in soluble nitrogen were not a satisfactory indication of the extent of protein breakdown.

The extractions were, therefore, repeated, using 2*M* calcium chloride and 0.1*M* acetic acid, which are better solvents for collagen than 0.1*N* sodium bicarbonate. Although the amounts of nitrogen extracted by both these solutions were rather greater than with bicarbonate, they were still not consistent with the visible degradation.

An attempt was therefore made to bring more degraded protein into solution using 5*M* acetic acid. This extracted over 20% of the nitrogen from the

TABLE II

SOLUBLE NITROGEN FOUND IN EXTRACTS OF CHROME AND VEGETABLE-TANNED LEATHERS

(*Soluble nitrogen as % of total nitrogen*)

Extractant	Chrome		Vegetable	
	Control	Deteriorated 15 weeks at 60°C.	Control	Deteriorated 10 weeks at 60°C.
0.1*N* $NaHCO_3$	0.5	1.5	0.5	1.5
2*M* $CaCl_2$				
nonvolatile	0.06	0.16	0.14	3.37
volatile	0.74	1.58	1.06	1.13
0.1*M* acetic acid				
nonvolatile	0.12	0.24	0.29	2.90
volatile	0.76	1.60	1.07	1.16
5*M* acetic acid				
nonvolatile	0.14	0.98	0.61	23.2
volatile	0.70	1.48	1.11	1.38

vegetable-tanned leather. Further determinations showed that the soluble nitrogen increased with the deterioration. Neutralization of the 5*M* acetic acid extracts precipitated a large proportion of the material. On paper electrophoresis of the extracts some separation was obtained. With the 5*M* acetic acid extracts most of the material stayed at the origin and stained with naphthalene black, while with the 0.1*M* extracts most of the material stained with ninhydrin. It would, therefore, seem that 0.1*M* acetic acid extracts mainly small peptides and amino acids and most of the volatile-nitrogen, while the 5*M* acetic acid, in addition, dissolves quite large protein fragments. The composition of these extracts and of the degraded protein as a whole are being examined. The volatile nitrogen probably consists mainly of ammonia and other simple compounds. It appeared, therefore, that extraction with these two solutions should give useful information on the protein breakdown.

All leathers were therefore extracted with these two solvents, and volatile and total nitrogen were determined (*see Fig. 5.*).

At 60°C. the soluble nitrogen extracted increased slowly with time of storage but only reached high values when degradation was extensive, that is, with the vegetable, semichrome, and retan leathers, with values of 21.2%, 14.1%, and 28.7% respectively. Increases in soluble nitrogen occurred most rapidly with the vegetable-tanned leather. With the chrome leather little was extracted even after storage for 15 weeks, although its strength had been reduced to 25% of the original value. Increases in volatile nitrogen were small except with the combination-tanned leathers.

At 40°C. increases in soluble nitrogen were smaller than at 60°C. although in many instances losses in strength on prolonged storage were similar to, or greater than, those occurring during the shorter periods at the higher temperature. Again, high values were only obtained when the leathers were beginning to show signs of gross deterioration. In the absence of mold both volatile and nonvolatile nitrogen were low in the vegetable- and chrome-tanned leathers, even after 72 weeks. Appreciably greater amounts of nitrogen were extracted from the combination-tanned leathers. Mold growth on the chrome- and vegetable-tanned leathers increased the volatile nitrogen but had little effect on the nonvolatile nitrogen. The total amounts of nitrogen extracted from the semichrome and retan leathers was slightly less in the presence of mold. With the semichrome leather the volatile nitrogen was, however, markedly increased at the expense of the nonvolatile. With the retan leather both volatile and nonvolatile nitrogen were decreased. The volatile nitrogen of the retan leather in the absence of mold was, however, particularly high.

Extraction of chrome tan.—The 5*M* acetic acid extracted about 60% of the chrome from the original chrome leather, but after a short time of storage at either temperature this had dropped to about 45%, and on further

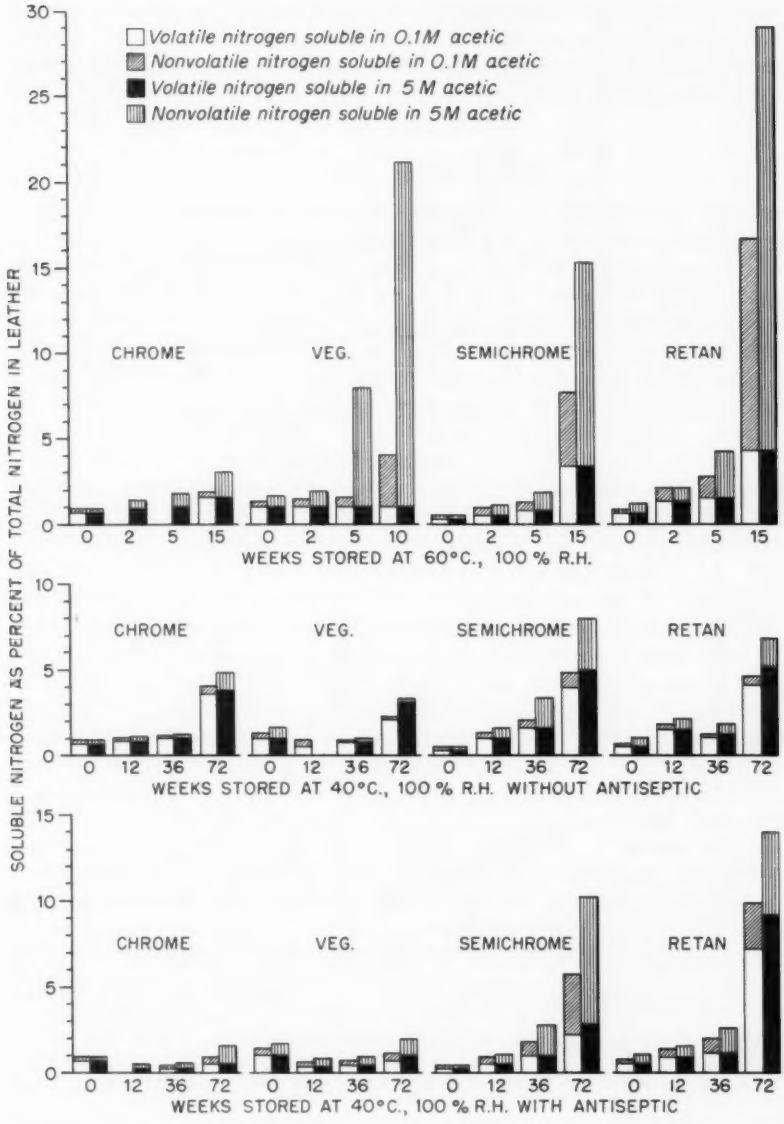
Volatile nitrogen soluble in 0.1M acetic
Nonvolatile nitrogen soluble in 0.1M acetic
Volatile nitrogen soluble in 5 M acetic
Nonvolatile nitrogen soluble in 5M acetic
SOLUBLE NITROGEN AS PERCENT OF TOTAL NITROGEN IN LEATHER
CHROME
VEG.
SEMICHROME
RETAN
0 2 5 15 0 2 5 10 0 2 5 15 0 2 5 15
WEEKS STORED AT 60°C., 100 % R.H.
0 12 36 72 0 12 36 72 0 12 36 72 0 12 36 72
WEEKS STORED AT 40°C., 100 % R.H. WITHOUT ANTISEPTIC
WEEKS STORED AT 40°C., 100 % R.H. WITH ANTISEPTIC

FIGURE 5.—Soluble, volatile, and nonvolatile nitrogen extracted from stored leathers by 0.1*M* acetic acid and 5*M* acetic acid.

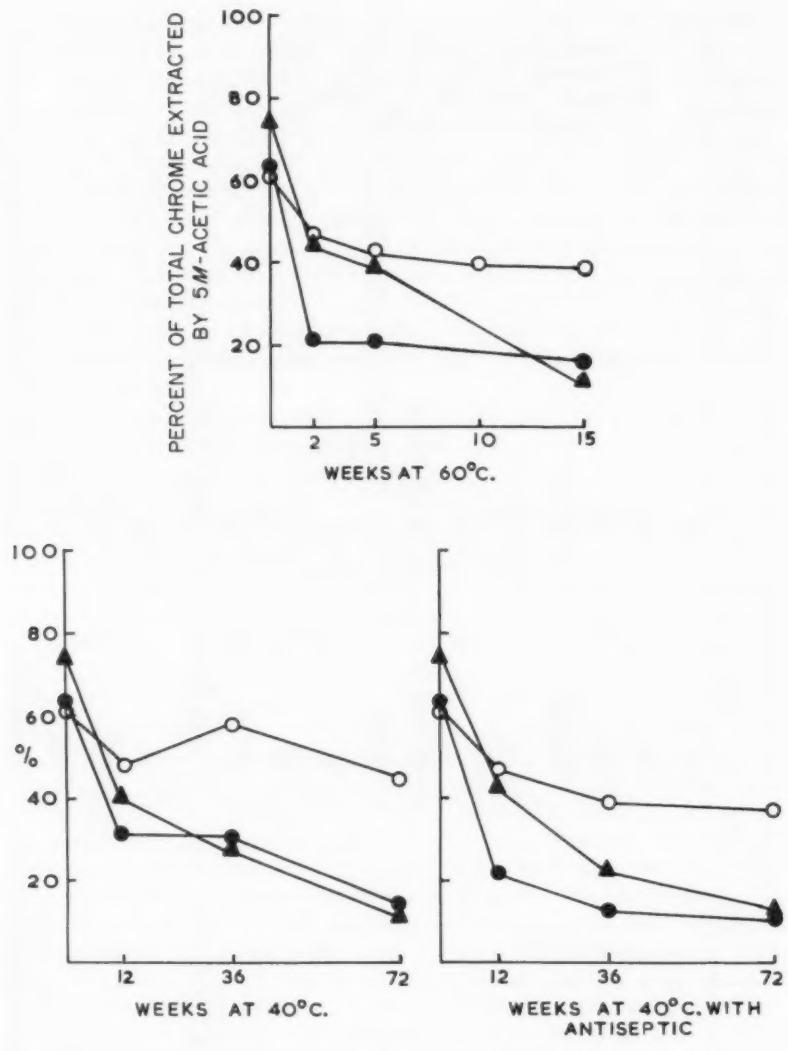

FIGURE 6.—Percentage of total chrome in leather extracted by 5*M* acetic acid.

○ ——— ○ Chrome-tanned
▲ ——— ▲ Semichrome
● ——— ● Chrome retan

storage it finally reached a steady value of about 40%. Even greater reductions in the chrome extracted were found with the semichrome and chrome retan leathers, less than 20% being soluble after the longest period of storage at either 60°C. or 40°C. (*see Fig. 6*), compared with 75% and 63% respectively in the original leathers.

DISCUSSION

The results of storage at 40°C. over water largely confirm those reported in Part I. The vegetable- and chrome-tanned leathers were fairly resistant to these conditions, but the combination-tanned leathers, although containing the same tans as the straight tannages, lost strength rapidly. The chrome-tanned leather was the only one on which the growth of mold had any observable effect. Kanagy *et al.* (4) also found relatively high losses in strength of a chrome leather on which mold had developed, but Roddy and Jansing (6) did not confirm this. It seems possible that there may be considerable differences between leathers or that particular molds are responsible. Further work is required to elucidate this behavior.

Although the general pattern of deterioration was the same at 60°C. as at 40°C., the relative behavior of the four types of leather was different. The chrome leather was still outstanding in its resistance, for although its strength was low after 15 weeks' storage, its appearance was still satisfactory. The vegetable-tanned leather, however, deteriorated rapidly, and after 10 weeks was more damaged than either of the combination-tanned leathers. This may be due to the fact that the temperature of storage was quite near the shrinkage temperature of the leather. Accelerated tests at 60°C. for the comparison of the stability of different types of leather are, therefore, not possible.

Some information regarding the breakdown of the protein can be deduced from the soluble nitrogen extracted. Hydrolysis of amide groups in the collagen would lead to increases in volatile nitrogen, but in many cases the amounts found exceed the maximum which would be expected from this source, i.e., about 2% of the total nitrogen. It appears, therefore, that deamination of amino acids must have occurred in some instances, particularly in the presence of mold. With the semichrome and retan leathers the losses of amino acids could amount to 5% of the total skin protein in the worst cases. No precautions were taken to avoid losses of volatile compounds during storage, but as the pH of the leathers was 4.0 or below, such losses seem unlikely. No appreciable change in nitrogen content of the leathers was detected.

The nonvolatile nitrogen probably consists mainly of peptides and amino acids. Increases did not necessarily follow losses in strength (*see also refs. 2, 3, and 14*). Relatively large losses in strength occurred without any appreciable increase in solubility, particularly with the chrome leather. High values were only obtained when the leathers were too weak to test, and their fiber structure was partially lost.

The glassy appearance of the middle layer of the leathers containing vegetable tan suggests that there may have been some degradation similar to the conversion of collagen to gelatin. Such changes in appearance did not occur at any stage with the chrome leather, and even under the microscope only slight evidence of damage could be seen. Other changes in the protein are not as extensive, and it seems likely that the mechanism of deterioration of this leather differs from that of leathers containing vegetable tans, in which oxidation and polymerization of the vegetable tan would also be expected to influence the deterioration.

The semichrome and chrome retan leathers behaved similarly to each other in general, suggesting that the order in which the two tanning processes were carried out was not important but that the presence of a chrome-vegetable tan complex was the controlling factor.

The effect of storage on the extractability of the chrome is difficult to explain. With the chrome leather it presumably indicates that the chrome complex had become more firmly fixed to the protein. This would also explain the increase observed in the shrinkage temperature. This explanation does not appear to apply to the combination-tanned leathers, in which the chrome tan was much less readily extracted, but the shrinkage temperature of the leather decreased. It seems likely that the chrome tan was removed from its complex with the collagen to form a more stable insoluble complex with the vegetable tan, as suggested in Part I. In the case of the retan leather stored for 15 weeks at 60°C., 5*M* acetic acid extracted 28.6% of the nitrogen of the leather, but only 15.8% of the chrome, suggesting that much of the chrome has been removed from the collagen and is present in a more insoluble complex.

It seems likely that the deterioration of the vegetable, semichrome, and retan leathers involves fairly extensive degradation of the protein. The results indicate that this may occur by at least two mechanisms, a hydrolytic breakdown of peptide chains and an oxidative mechanism probably involving deamination of the amino acids. In addition it is possible that there is a loss of molecular structure similar to the partial conversion of collagen to gelatin. With chrome leather the changes in the protein are small, perhaps because the few stable cross links formed are more effective in preventing disorganization of the protein molecule than the cross links in the other leathers.

Further information on the oxidative and hydrolytic breakdown of the protein in both leather and untanned skin is being sought.

ACKNOWLEDGMENTS

Thanks are due to Dr. H. E. Nursten of the Leather Industries Dept., Leeds University, and Dr. J. H. Bowes of British Leather Manufacturers' Research Association for helpful discussion during the course of the work; also to Mr. G. B. Shooter for many of the analytical determinations.

The author also wishes to thank the Director and Council of British Leather Manufacturers' Research Association for the grant of a Research Fellowship while at Leeds.

REFERENCES

1. Bowes, J. H., and Raistrick, A. S. Part I.
2. Kanagy, J. R., and Tobias, P. E. *JALCA*, **37,** 426 (1942).
3. ———, Charles, A. M., Abrams, E., and Tener, R. F. *JALCA*, **41,** 198 (1946).
4. ———, Seebold, R. E., Charles, A. M., and Cassell, J. M. *JALCA*, **44,** 270 (1949).
5. Lollar, R. M. *JALCA*, **49,** 605 (1954).
6. Roddy, W. T., and Jansing, J. J. *JALCA*, **49,** 773 (1954).
7. Mitton, R. G., and Turner, J. N. *J. Soc. Leather Trades Chemists*, **39,** 343 (1955).
8. Mann, C. W., and Steiner, E. T., quoted by Seligsberger, L., and Mann, C. W., in *Chemistry and Technology of Leather Manufacture* Vol. II (New York: Rheinhold, 1958) 489.
9. Seligsberger, L., Mann, C. W., and Clayton, H. *JALCA*, **53,** 627 (1958).
10. Mitton, R. G., and Wyatt, K. E. Unpublished work.
11. Sykes, R. L., and Williams-Wynn, D. *J. Soc. Leather Trades Chemists*, **43,** 265 (1959).
12. *Official Methods of Analysis.* Society of Leather Trades Chemists, Croydon, 1957.
13. Chibnall, A. C., Rees, M. W., and Williams, E. F. *Biochem. J.*, **37,** 354 (1943).
14. Mann, C. W., Steiner, E. T., Clayton, H., and Seligsberger L. *JALCA*, **54,** 680 (1959).

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Oil tannage seems the first real tanning process applied in prehistoric Europe. The hide's own fats, marrow, brains, milk, cod-liver oil and fish oils seem to have been used. Probably combinations of smoke and oil tannage were in use too. Oil tannage certainly arose from the operations for obtaining a supple hide in which the hide's own fats were supplemented by brain stuff, marrow and the like, which were then rubbed and beaten into hide, often supplemented by chewing (which helps to emulsify the fats with saliva). The pure air of the mountain caves was certainly very suitable for such processes.

In coastal regions fish-oils could easily be substituted for marrow and brains. Whale-oil may have been used sometimes, though it did not become generally available before the ninth century A.D., when whaling started. Yolk of egg may have been used in later days when poultry became common in Central Europe and the West. Milk and butter are used for oil tanning by Asiatic nomad tribes, milk being the mordant and butter the fatty material to impregnate the skin, for kid-leather they use yolk of egg. Fine flour is sometimes used too, North-American Indians use maize-flour, and the brains of caribou deer. The leather obtained by this oil tanning is very supple and stable against rotting and water.—R. J. Forbes. "Leather in Antiquity" in *Studies in Ancient Technology*, Vol. V (Leiden, the Netherlands: E. J. Brill, 1957).

THE ACTION OF HEAT AND MOISTURE ON LEATHER

PART III. THE EFFECT OF pH ON THE DETERIORATION OF VEGETABLE, CHROME, SEMICHROME, AND CHROME RETAN LEATHERS*

J. H. Bowes and A. S. Raistrick

British Leather Manufacturers' Research Association, Milton Park, Egham, Surrey, England.

ABSTRACT

Vegetable, chrome, semichrome, and chrome retan leathers were adjusted to various pH values in the range 2 to 9 and stored at 40°C. over water for 15 weeks.

The strength of the leathers as measured by buckle tear load was little affected by the adjustment of pH except when this was reduced below 3.0. Losses in strength during storage varied with the type of leather and with its pH. In general, in the range 4 to 8 pH had little effect on the losses of strength of chrome, vegetable, and semichrome leathers, but with the retan leather losses increased progressively with fall in pH. In this range the chrome leather lost no strength, the vegetable-tanned leather about 30%, the semichrome about 50%, and the chrome retan leather 10% at pH 8.0, increasing to 25% at pH 4.0. At lower pH values the losses in strength of the chrome and retan leathers increased sharply but those of the semichrome only slightly, while with the vegetable-tanned leather, losses were only increased at the lowest pH value (2.0). At this pH, however, the vegetable-tanned leather was extensively damaged after only two weeks' storage.

The leathers containing vegetable tan became progressively darker in color with increasing pH and tended to become cracky, but the chrome-tanned leather was relatively unaffected both in appearance and feel.

It is concluded that for resistance to storage the pH of the leather should be above 3.5, and even higher with chrome leather and retan leather. High pH values, however, lead to darkening of leathers containing vegetable tannins and to detannage of chrome leather, so that a limit must be set. In wear, the absorption of perspiration increases the pH of the leather, and this must also be borne in mind.

*The work reported in this paper forms part of a research program sponsored by the U. S. Department of Agriculture under the authority of U. S. Public Law 480.

INTRODUCTION

The effect of exposure of a variety of leathers to the action of moist heat has been described in Parts I and II (1,2). With the exception of chrome upper and gloving, most types of leather were found to lose strength, but only in extreme cases was there any marked increase in solubility. Although it was not possible to correlate losses in strength or change in other properties of any particular type of leather with its pH, it seems reasonable to assume that this must be a factor. In particular it would be expected that hydrolytic breakdown of the collagen would increase as the pH of the leather is decreased.

Little evidence on the effect of pH on the deterioration of leather under warm moist conditions appears to be available. The absorption of acid is known to accelerate the deterioration of upholstery and bookbinding leathers (3,4), and Kanagy, Seebold, Charles, and Cassel (5) have shown that in some cases raising the pH of chrome- and vegetable-tanned leather reduced deterioration under warm moist conditions.

The pH of any one type of leather may vary between quite wide limits, and in wear the absorption of perspiration may cause increases of two or more pH units. In order to be able to predict the probable behavior of a leather in wear it is, therefore, necessary to know how such changes in pH are likely to affect their resistance to the action of moist heat. Little information appears to be available on this point, though the work of Mitton and Wyatt (6) suggests that increases in pH due to synthetic and natural perspiration reduce losses in strength of vegetable, chrome, semichrome, and chrome retan leathers stored wet at 40°C. Four leathers, vegetable, chrome, semichrome, and chrome retan, have, therefore, been adjusted to various pH values, and their subsequent behavior on moist storage has been examined.

EXPERIMENTAL

Samples of vegetable, chrome, semichrome, and chrome retan leathers were adjusted to twelve pH values between 2 and 9 and stored at 40°C. over water for 15 weeks. The leathers were the same as those used in a previous experiment and have already been described (2). Samples 6″ x 1″ were cut from the britch end of the leathers in six blocks of twelve, and one sample from each block was allotted at random to each of the twelve treatments.

For adjustment of pH the samples were placed in a screw-top bottle of such depth that the samples just fitted below the shoulder. A volume of hydrochloric acid or sodium carbonate solution of the concentrations shown in Table I was added in the proportion of 1 ml. per gram of leather, and the bottles were rotated on their sides intermittently for 24 hours. During this time between 75% and 90% of the solutions were taken up by the leathers. The amounts of acid and alkali to be used to give a suitable range of pH were predetermined in a preliminary experiment. One percent p-nitrophenol was

TABLE I

CHANGE IN pH ON STORAGE

Treatment	Vegetable		Chrome		Semichrome		Retan	
	Before	After	Before	After	Before	After	Before	After
1. *N* HCl	1.90	2.30	2.32	2.42	1.92	2.19	1.86	2.14
2. 0.2*N* HCl	2.77	2.76	3.42	3.39	2.35	2.47	2.39	2.52
3. 0.1*N* HCl	3.38	3.12	3.74	3.37	2.63	2.69	2.64	2.68
4. Water	4.42	3.73	3.98	3.64	2.90	2.84	2.99	2.84
5. 0.05 *N* Na_2CO_3	4.60	3.66	4.16	3.33	3.14	2.88	3.12	2.94
6. 0.1*N* "	4.97	4.10	4.22	3.58	3.32	2.91	3.32	3.06
7. 0.15*N* "	5.14	4.26	4.31	3.83	3.56	3.20	3.42	3.15
8. 0.25*N* "	5.78	4.80	4.72	4.11	4.12	3.52	4.02	3.42
9. 0.4*N* "	6.12	5.26	5.92	4.27	5.24	3.98	4.75	3.95
10. 0.6*N* "	6.32	5.62	6.22	4.66	5.91	5.27	5.27	4.67
11. 0.8*N* "	6.68	5.87	6.99	5.17	6.64	6.04	6.66	5.80
12. 1.5*N* "	7.60	6.45	8.99	7.07	7.78	6.85	7.80	7.06

added to each of the solutions to reduce mold growth during subsequent storage.

The leathers were dried out on glass plates, and the strength (buckle tear load) was determined. The torn strips were cut off, and the pieces were used for the determination of pH of water extract and shrinkage temperature.

The leathers were then suspended over water in closed glass vessels and stored at 40°C. in an incubator for 15 weeks. After storage the pieces were dried out on glass plates, conditioned, and tested for buckle tear load, pH, and shrinkage temperature. They were also assessed for color and crackiness.

Methods.—Shrinkage temperatures were determined in water or 75% v/v glycerol-water mixture with specific gravity 1.194 using a counterweight of 10 g. The pieces were wetted first in water under reduced pressure, and the rate of heating was 2° per minute. The temperature at which shrinkage was first observed was taken as the shrinkage temperature. For pH of water extract, 2.5 g. leather in the form of pieces about 3 mm. sq. were extracted with 50 ml. distilled water for 48 hours with occasional shaking. Nitrogen soluble in 5*M* acetic acid was extracted and determined as described by Raistrick (2).

Buckle tear loads were determined by the usual procedure (7) after conditioning at 21°C. and 70% R.H. The three tests made on each sample were made at 1" intervals from each other along the strip. The percentage loss in strength at each stage and the mean losses for the six samples were calculated. Percentage losses in strength of replicate varied by ±15%.

RESULTS

Effect of pH adjustments.—After treatment, the pH of water extracts of the leathers lay within the range 1.9 to 9.0. Although the values varied appreciably for the four types of leather, no obvious differences in their buffering capacities were apparent.

The appearance of the chrome-tanned leathers was little affected except that those given the more alkaline treatment had a greenish tinge. The leathers containing vegetable tan became progressively stiffer and darker in color with increasing alkalinity above pH 4.0. Even at the highest pH value, however, the leathers were not excessively stiff. These effects were most marked with the vegetable leather and least marked with the semichrome.

The strength of the leathers was not greatly affected by adjustment of the pH to values in the range 3 to 8, in most cases a slight increase being observed (*see Figs. 1–4*). At lower pH values strength was reduced, and after adjustment to pH 2.0 the chrome leathers had lost nearly 20%, and the vegetable, semichrome, and retan leathers between 30% and 40%, of their strength. Percentage changes in strength of replicates varied by ± 15%.

The shrinkage temperature of the retan and semichrome leathers was little affected by the treatment, but that of the vegetable and chrome leathers was reduced by the two most acid treatments (Table II). The shrinkage temperature of the chrome leather also decreased as the pH of the leather was raised above 5.0 (*see also Bowes and Moss* [8]). There was some indication that the semichrome and retan leathers were similarly affected at the highest pH.

Effect of moist storage.—In spite of the addition of p-nitrophenol to the solutions used in adjusting the pH, varying degrees of mold growth were observed on the leathers after six weeks. In general, this was most prevalent at the intermediate pH values and on the vegetable-tanned leathers. The mold was removed from the leathers, and beakers of toluene were placed in the storage vessels. This checked any further extensive growth of mold.

During storage the pH of the leathers tended to revert toward the original pH of the leather (*see Table I*), presumably because equilibrium had not been reached during the treatments. With the chrome, semichrome, and retan leathers the changes probably also reflect changes in the chrome complex.

Appearance of leathers.—The appearance of the chrome leather was not appreciably affected by the storage, except for a slight enhancement of the green tinge observed after adjustment to the more alkaline pH values. The most acid vegetable and retan leather showed signs of extensive damage and had to be removed after two and six weeks' storage respectively. These samples were darkened in color, hard, and brittle, and the middle layer was dark and glassy in appearance and had lost all fiber structure. In general, the darkening in color and increased stiffness observed after the

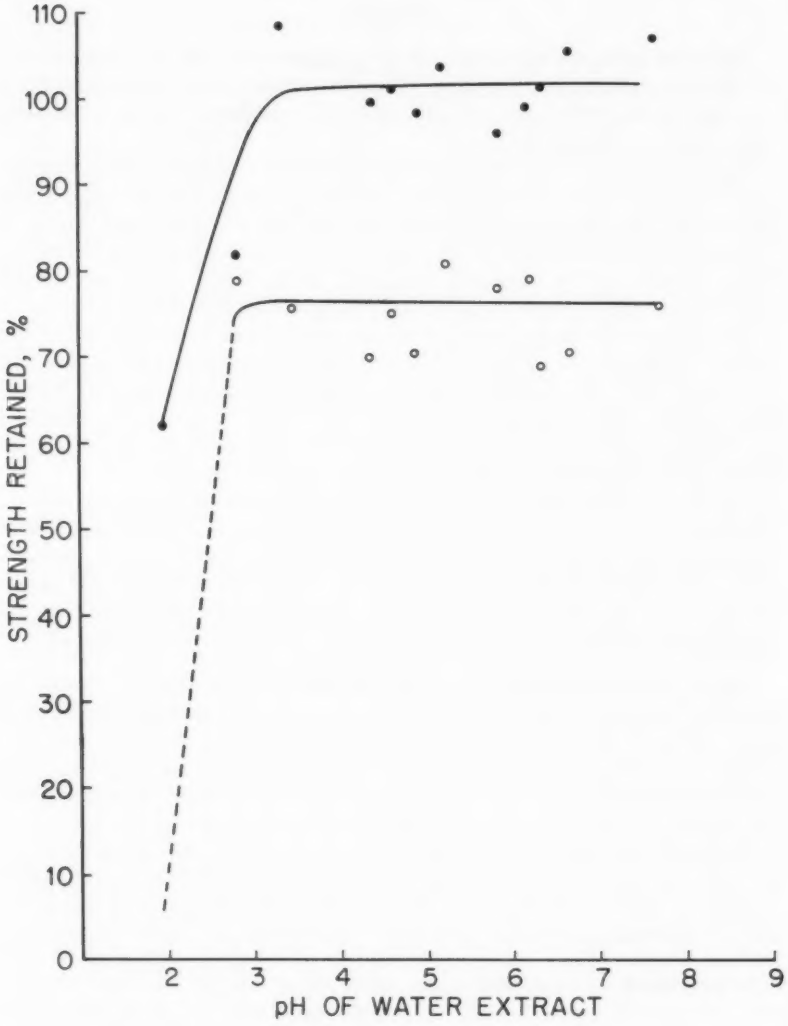

FIGURE 1.—Influence of pH on strength. Vegetable-tanned leather.

●——● Changes in strength on adjustment of pH. Buckle tear load after treatment as a percentage of buckle tear load of original leather.

○——○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

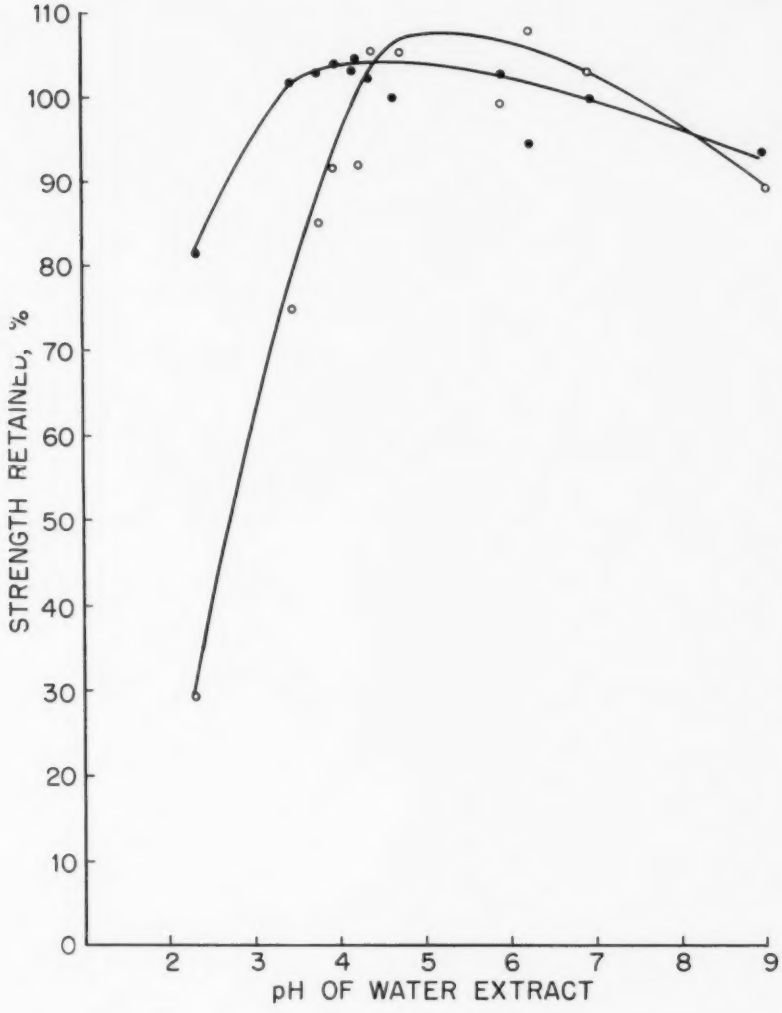

FIGURE 2.—Influence of pH on strength. Chrome-tanned leather.

●——● Changes in strength on adjustment of pH. Buckle tear load after treatment as a percentage of buckle tear load of original leather.

○——○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

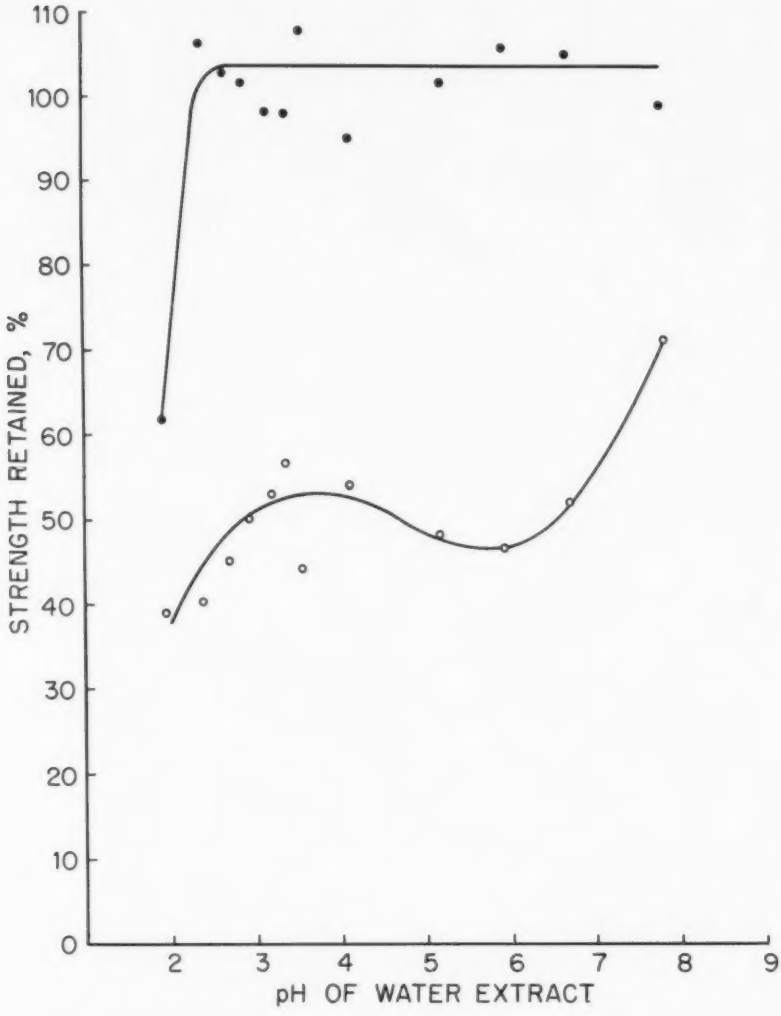

FIGURE 3.—Influence of pH on strength. Semichrome leather.

●——● Changes in strength on adjustment of pH. Buckle tear load after treatment as a percentage of buckle tear load of original leather.

○——○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

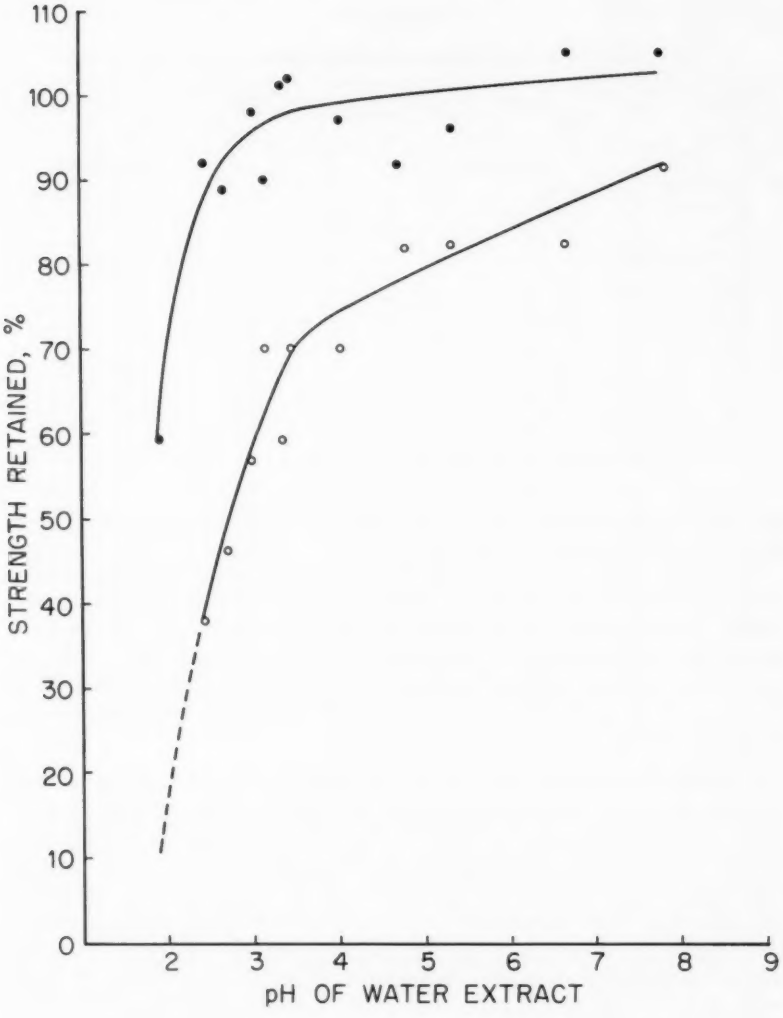

FIGURE 4.—Influence of pH on strength. Chrome retan leather.

●——● Changes in strength on adjustment of pH. Buckle tear load after treatment as a percentage of buckle tear load of original leather.

○——○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

TABLE II

CRACKINESS AFTER STORAGE

Treatment	Vegetable	Chrome	Semichrome	Retan
1. *N* HCl	+++++ very damaged	0	++++	+++++ very brittle
2. 0.2*N* HCl	+	0	++	++
3. 0.1*N* HCl	0	0	++	++
4. Water	0	0	+	+
5. 0.05*N* Na_2CO_3	0	0	+	++
6. 0.1*N* "	0	0	+	++
7. 0.15*N* "	0	0	++	++
8. 0.25*N* "	++	0	+++	+
9. 0.4*N* "	+	0	+++	+
10. 0.6*N* "	+	0	++++	++
11. 0.8*N* "	++	0	++++	++
12. 1.5*N* "	++++	+	++++	++

0 = not cracky
+ — ++++++ = "very slightly" increasing to "very cracky"

more alkaline treatments were accentuated by storage, and in many cases the leathers had become cracky (*see Table II*).

The chrome leather showed no tendency to crack except at the highest pH value. The most acid vegetable, semichrome, and retan leathers were all very cracky. The vegetable-tanned leather tended to become cracky at pH values above about 5.0, but only the most alkaline leather was very cracky. All the semichrome and retan leathers developed some degree of crackiness; the semichrome was the most affected, and as the pH rose above 4.0 it became increasingly cracky.

Shrinkage temperature.—As in previous experiments the shrinkage temperature of the vegetable-tanned leather tended to increase slightly during storage (1,2), but there was no evidence that this increase was affected by pH. The changes in shrinkage temperature of the chrome leather were somewhat erratic, but in most cases there was a rise. The shrinkage temperature of both the semichrome and retan leathers fell markedly during storage. The semichrome leathers were the most affected, the fall in shrinkage temperature generally being about 16°, increasing to 23° at the highest pH and to as much as 49° at the lowest pH. With most of the retan leathers falls were between 10° and 16°, increasing to 36° at the lowest pH and becoming negligible above pH 4.5.

Buckle tear load.—The strength retained after storage, expressed as percentage of the strength immediately after adjustment of the pH, is plotted against the pH of the leathers in Figs. 1 to 4. Replicates again varied by ±15%.

TABLE III

CHANGE IN SHRINKAGE TEMPERATURE DURING STORAGE, °C.

Treatment	Before	After	Change	Before	After	Change
		Vegetable			*Chrome*	
1. *N* HCl	60	62	+2	96	97	+1
2. 0.2*N* HCl	69	73	+4	106	108	+2
3. 0.1*N* HCl	77	76	−1	110	110	0
4. Water	77	78	+1	110	107	−3
5. 0.05*N* Na_2CO_3	79	81	+2	112	106	−6
6. 0.1*N* "	77	81	+4	112	108	−4
7. 0.15*N* "	77	82	+5	114	111	−3
8. 0.25*N* "	79	82	+3	108	113	+5
9. 0.4*N* "	78	83	+5	101	111	+10
10. 0.6*N* "	78	81	+3	95	106	+11
11. 0.8*N* "	76	79	+3	88	94	+6
12. 1.5*N* "	77	74	−3	63	70	+7
		Semichrome			*Chrome Retan*	
1. *N* HCl	109	66	−49	98	62	−36
2. 0.2*N* HCl	109	88	−21	97	77	−20
3. 0.1*N* HCl	109	93	−16	96	82	−14
4. Water	108	94	−14	96	86	−10
5. 0.5*N* Na_2CO_3	109	93	−16	96	86	−10
6. 0.1*N* "	109	93	−16	98	86	−12
7. 0.15*N* "	110	94	−16	100	84	−16
8. 0.25*N* "	109	95	−14	100	88	−12
9. 0.4*N* "	110	95	−15	99	91	− 8
10. 0.6*N* "	111	92	−19	96	96	0
11. 0.8*N* "	110	88	−22	94	94	0
12. 1.5*N* "	104	81	−23	93	86	− 8

The strength of the chrome leathers adjusted to pH values between 4.5 and 7.0 was little affected by storage, but losses in strength increased progressively with fall in pH below 4.5 until at pH 2.2 the leather only retained 30% of its strength before storage. There was also some loss in strength at the highest pH value.

Losses in strength of the vegetable-tanned leather were unaffected by variations in the pH in the range 2.5 to 8.0, fluctuating between 20% and 30%. Although adjustment of the pH to 2.8 in itself caused a marked reduction in strength, the further reduction on storage was only of the same order as that at the higher pH values. The deleterious effect of higher acidities was, however, apparent at pH 2.0, the leather being extensively damaged after only two weeks' storage.

The behavior of the semichrome leather was also relatively unaffected by pH, and even at the lowest pH value losses in strength were only slightly

greater than at the high values. The smaller loss in strength at the highest pH requires further investigation. With the retan leather losses of strength increased with decrease in pH over the whole range, slowly at first and then more rapidly below pH 4.0. As with the vegetable-tanned leathers the combined effect of adjustment to pH 2.0 and storage led to extensive loss of fiber structure and the collapse of the leather during storage.

Solubility in 5*M* acetic acid.—As in the previous investigation (2) the nitrogen extracted by 5*M* acetic acid was relatively small except with the most damaged leathers. With the vegetable, semichrome, and retan leathers both volatile and nonvolatile nitrogen were greatly increased by

TABLE IV

SOLUBLE NITROGEN

(*Nitrogen extracted by 5*M *acetic acid as percent total nitrogen*)

Treatment	Vegetable		Chrome		Semichrome		Chrome Retan	
	Volatile	Non-Volatile	Volatile	Non-Volatile	Volatile	Non-Volatile	Volatile	Non-Volatile
Original leather before storage	1.11	0.61	0.70	0.14	0.37	0.15	0.58	0.57
1. *N* HCl	3.77	14.49	0.60	0.44	1.08	6.03	2.12	27.39
2. 0.2*N* HCl	0.21	0.76	0.25	0.19	0.64	0.84	0.25	2.48
7. 0.15*N* Na_2CO_3	0.12	0.14	0.11	0.25	0.08	0.21	0.19	0.30
12. 1.5*N* Na_2CO_3	0.09	0.17	0.07	1.18	0.21	0.68	0.05	0.11
Same leather after storage for 12 weeks at 40°C. (no treatment—taken from ref. [2])	0.27	0.48	0.16	0.20	0.51	0.61	0.98	0.46
Same leather after storage for 10 weeks at 60°C. (from ref. [2])	1.40	19.8	1.55	1.50	4.36	11.76	4.25	24.4

storage at the lowest pH value (*ca.*2.0) but only slightly increased at the next lowest pH (*ca* 2.5–2.7). Of these the retan leather was the most affected, and the semichrome the least. The amounts extracted from the leather of pH 2.0 were of the same order as those extracted from the original leathers when stored for a similar period at 60°C. (2). The solubility of the chrome leather was not greatly affected by the pH of the leather during storage except for a slight increase with the leathers of lowest and highest pH.

DISCUSSION

The adjustment of the pH had some effect on the properties of the leather, increase in pH causing darkening and stiffening of the leathers containing

vegetable tans and decrease in pH causing some loss in strength. Except with the most acid leather, however, these changes were small compared with those occurring during storage.

The pH of the leathers had less effect on the changes taking place during storage than was expected. Only with the retan leathers did losses in strength decrease consistently with increase in pH over the whole range covered. With the chrome leathers the effect of pH was only obvious below pH 4.0; with the vegetable-tanned leather, only at the lowest pH; and with the semichrome leathers, it had only a slight effect even at pH 2.0.

Although increase in pH above 4.0 had little effect on the strength of vegetable and semichrome leathers, it had an adverse effect on their color and increased their tendency to develop crackiness, especially the semichrome leathers. The retan leather also darkened with rise of pH, but there was little variation in crackiness.

The effect of pH on the fall in shrinkage temperature of the semichrome and retan leathers is of interest. With leathers of low pH the falls are very great, resulting in final values approaching the danger level. The shrinkage temperature of the semichrome leathers also fell by about 20° at the two highest pH values, but in contrast that of the retan leathers of pH 4.5 and above fell little, if at all.

The increased solubility of the leathers in acetic acid solutions suggest that hydrolytic breakdown has been increased by lowering the pH, though with the chrome leathers this increase is relatively small.

How far these results are applicable to other vegetable, chrome, semichrome, and chrome retan leathers is not certain, but they give some indication of the pH range likely to give optimum resistance to moist heat. These vary slightly with the leather. With chrome leather it would seem that it is desirable to have a pH of water extract in the range 4.5 to 6.0. With the leathers containing vegetable tan, the upper pH is limited by the tendency to crackiness, particularly with the semichrome leathers. With vegetable-tanned leathers and semichrome leathers the pH should not fall below 3.0, and with retan leathers it should be as high as is consistent with a good color. The pH, however, is likely to change in wear; exposure to moist heat generally causes the pH to fall (1, 2), especially with semichrome and retan leathers, while absorption of perspiration may cause the pH to rise. The pH at which to aim will, therefore, be to some extent dependent on the purpose for which the leather is required.

As in previous investigations (1) chrome leather appears to be the most resistant to moist heat, changes but slightly in appearance, has little tendency to become cracky, and provided the pH is above 4.5, has small losses in strength. Chrome leather is, however, more susceptible to the detanning action of perspiration, and in some circumstances where perspiration is likely to be an important factor semichrome or retan leathers may be preferable.

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REFERENCES

1. Bowes, J. H., and Raistrick, A. S. Part I.
2. Raistrick, A. S. Part II.
3. *Progress on Leather Science* 1920–1945. British Leather Manufacturers' Research Association, London, 1948, p. 426.
4. Mann, C. W., and Steiner, E. T., quoted by Seligsberger, L., and Mann, C. W. in *Chemistry and Technology of Leather*, Vol. II (New York: Rheinhold, 1958) 489.
5. Kanagy, J. R., Seebold, R. E., Charles, A. M., and Cassel, J. M. *JALCA*, **44**, 270 (1949).
6. Mitton, R. G., and Wyatt, K. E. *Das Leder*, **12**, 285 (1960).
7. *Official Methods of Analysis*. Soc. Leather Trades Chemists, 1957, p. 178.
8. Bowes, J. H., and Moss, J. A. *J. Soc. Leather Trades Chemists*, **44**, 419 (1960).

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The Romans were great makers and users of leather. Their guilds included leather-dressers and makers of straps, harness, shields, wine- and oil-bags, and footwear. Roman footwear closely followed Greek models but developed an individual sturdiness for military use. It was produced in large quantities in organized factories, and a substantial export trade grew up. The caliga of the foot-soldier had a thick sole of two or more layers of vegetable-tanned hide sewn or laced together and studded with iron nails or spikes. The upper consisted either of a system of straps or a kind of lace-up sock which left the toes bare. The cutting-out was done, as we learn from paintings and sculpture, with the half-moon knife. Whereas ordinary footwear appears usually to have been black, that for the aristocracy was frequently brightly coloured—yellow, red, and green. Purple was reserved for imperial use. It is probable that the dyes were employed upon alumed leather.—John W. Waterer. "Leather" in *A History of Technology*, Vol. II, ed. Singer, Holmyard, Hall and Williams (Oxford, University Press, 1957).

THE UPTAKE OF VEGETABLE TANNING MATERIALS BY CHROMED HIDE SUBSTANCE

K. H. GUSTAVSON

Garverinäringens Forskningsinstitut
Stockholm, Sweden

ABSTRACT

The differences in findings by earlier investigators and by Kanagy as to the uptake of vegetable tanning materials by prechromed collagen are not real but due to an oversight. Kanagy's data pertain to the *total uptake* of the constituents of *vegetable tanning extracts*, whereas in the earlier studies the amounts of *irreversibly fixed tannins* have been estimated.

While the *irreversible tannin fixation* by collagen is markedly *increased* by pretanning with cationic chromium salts, the amounts of *combined water solubles* and sorbed matters are appreciably *reduced* with increasing chrome content of the collagen. Hence, some of the theoretical conclusions drawn are not justified.

Kanagy's criticism of the mode of ascertaining the amounts of fixed tannins in earlier studies, i.e., as the difference between 100 and the sum of total ash (including Cr_2O_3), total sulfate, and collagen, is unfounded. Actually, the results thus obtained agree closely with the figures given by the mode of assessment he prefers. The Kubelka factor for converting the amount of Cr_2O_3, found on analysis of the combination-tanned leather, to the "chrome complex" is proven to give grossly faulty values of the amounts of vegetable tanning material taken up by the chromed hide substance and to be useless for combination-tanned leather. The widely different composition of the chrome complexes of leathers after vegetable retannage, according to the type of extract, pH value, time of tanning, and other factors, precludes the use of a specified conversion factor for estimating the analytically nondeterminable part of the chrome complexes.

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INTRODUCTION

In a recent, most interesting paper by Kanagy (1) on the retannage of chrome-tanned hide powder and pelt with vegetable tanning materials, the findings are compared with the results of some of the earlier studies of this complicated tannage, which has attained great technical importance since the time of the earliest systematic investigation (2).

However, some of the statements in Kanagy's paper cannot be accepted and cannot remain unchallenged. The aim of this note is to uncover the reasons for the points of disagreement between Kanagy's observations and statements and the findings in earlier investigations (2–12).

The key to the differences in the findings of Kanagy and those in the earlier investigations noted above, claimed by Kanagy (1), is not to be found in the experimental results. Actually, the explanation of the divergencies is that two different types of processes are compared: The *total uptake* of the *vegetable tanning material* is the object of Kanagy's study, whereas the *irreversible fixation* of *vegetable tannins* is the main theme of the investigations cited (2–12).

It is evident from the description of the washing procedure given in Kanagy's paper that the retanned stock was lightly washed only (three washings with water at room temperature). This is further brought out by the figures for "tannin" on hide-substance basis which for the wattle bark extract attain such great values as 105 (Table VIII[1]) for calfskin, whereas for calfskin pelt values of the order of 60 for the irreversibly fixed tannins, on hide-substance basis, are normal under comparative experimental conditions. The vegetable-tanned specimens of intact hide and chromed hide powder in my series of investigations, commencing with the 1927 paper (2), were thoroughly washed until a negative ferric chloride test was obtained; in later studies this test was complemented by a negative gelatin test of the water after shaking 2-g. (of collagen) portions of the vegetable-tanned hide powder in 500 ml. of water for one hour at room temperature (8). The vegetable tanning matter fixed by the collagen and by the chromed collagen after this thorough washing, lasting at least 24 hours, was considered to be *irreversibly* fixed, in regards to water under the given experimental conditions.

Page and Holland (3) applied the Wilson-Kern method for estimation of the irreversibly bound tannins in the vegetable-tanned and vegetable-retanned specimens. Page (13) differentiated between (*a*) irreversibly combined tannins, (*b*) combined water solubles, and (*c*) free water solubles. Kanagy's mode of washing would likely remove the free water solubles only. In the study of Burton and Vivian (7), the Page method (13) of differentiation of the various fractions was applied, the main attention in their discussion being given to the irreversibly fixed tannins. These authors as well as van Vlimmeren (5) have also used organic solvents for the removal of tanning matter from the tanned hide powder for further differentiation of the degree of stability of the irreversibly fixed fraction.

EFFECT OF THE CHROME CONTENT ON THE VEGETABLE RETANNAGE

The effect of the prechroming, and particularly the chrome content of the collagen upon its uptake and binding of the various constituents of vegetable tanning materials, is the cardinal point in the present survey. The main

part of the studies (2–12) have been carried out with wattle bark extract, using hide powder as the substrate. Therefore, in Kanagy's paper the series with that extract are of interest primarily, as are also the main series with sulfited quebracho extract, since this type of condensed tannin behaves similarly to the wattle extract. While the series with pelt are important from the technical point of view, they cannot be included in the present discussion in view of the fact that the diffusion plays a prominent role, i.e., the rate factor. Hence, the data from the hide powder experiments in Kanagy's paper (1) will serve for comparison with the data from the earlier investigations with hide powder (2–12). In all the publications cited, it is found that the *irreversible fixation of tannins* by collagen is largely increased by its prechroming, the increase being a function of the chrome content of the substrate up to certain limits (2, 3, 4, 7, 8, 12), although the trends of the tannin fixation with increasing chrome content show marked differences in the papers cited.

In the most important contributions of Page and Holland (3) it was found that the uptake of combined water solubles decreased linearly with the augmented degree of prechroming. Figure 1 illustrates the reaction of hide powder which had been chromed to different degrees with the constituents of a solution of wattle extract. The curve for the irreversible binding of the tannins rises steadily with the degree of prechroming. The uptake of combined water solubles follows a linearly descending curve. The total uptake of the vegetable tanning materials exhibits a slight increase of the uptake with increasing chrome content of the hide powder. Burton and Vivian (7) found a very steep linear increase of the irreversible fixation of the tannins in wattle extract up to the highest chrome contents of the collagen. Like Page and Holland, they report that uptake of the combined water solubles was greatly reduced by augmented chrome content of the collagen, as would be expected since the total uptake of the constituents of the tanning extract was practically independent of the chrome content of the hide substance. As already mentioned, in Kanagy's paper two entirely different types of removal of vegetable tanning matters by collagen are compared. In view of this fact, some of the statements and claims in that paper are invalidated.

In some respects, e.g., as to the reaction kinetics, Kanagy's findings confirm earlier reported results. Thus, the uptake of the vegetable tanning materials (the total as well as the irreversibly fixed portions) by chromed hide substance occurs at two different rates: (*a*) a rapid reaction without any displacement of complexly held sulfate groups in the chromium complexes, and (*b*) a gradually occurring uptake of vegetable tanning material whereby some of the sulfato groups are displaced. (*Cf.* Fig. 5 in ref. 1 with pelt, and Fig. 4 in ref. 8 with hide powder, both for wattle bark extract.)

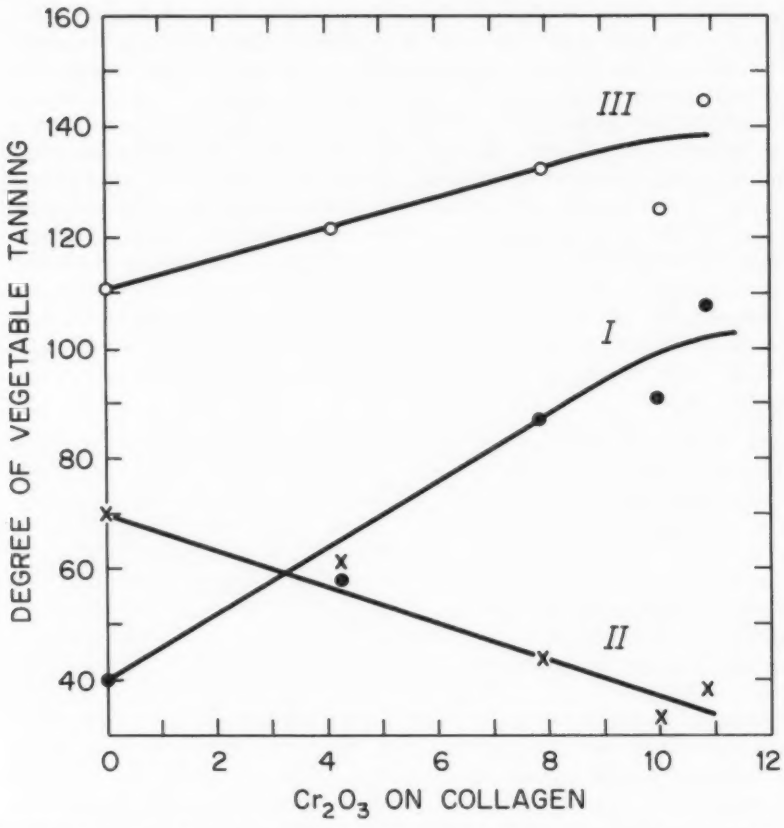


FIGURE 1.—The effect of the degree of prechroming of hide powder upon the irreversible fixation of tannins and the uptake of water solubles and total tanning matter from wattle bark extract.

Ordinate: g. of vegetable tanning matter combined with 100 g. of collagen.
Abscissa: g. of Cr_2O_3 on 100 g. of collagen in the chromed hide powder.

I. Irreversibly fixed tannin
II. Combined water solubles
III. Total tanning matter

UPTAKE OF VARIOUS EXTRACTS

As to the influence of the degree of prechroming of collagen upon its uptake of constituents of vegetable tanning extracts, the data of Otin and Alexa (14), cited by Kanagy, relate to the total uptake of the extracts (combined

water solubles + irreversibly fixed tannins) also. Such information is also to be found in the papers by Page and Holland (3) and by Burton and Vivian (7) for wattle extracts. Otin and Alexa include data on a number of extracts. A still wider array of data for the irreversible fixation of vegetable tannins by chromed hide powder are available for some twenty different tanning extracts in publications by Rao and the present author (12, 15). In this context it should only be noted that the tannins of the hydrolyzable type, e.g., tannic acid, show the smallest increase of the *irreversible* fixation by the prechroming of the collagen, while the binding of the tannins of the condensed class, such as those of wattle and sulfited quebracho extracts, is greatly augmented. A comparison with Kanagy's data on the total *sorption* of these extracts shows a similar trend, although the combined water soluble fraction, a negative factor in this instance, will tend to level the differences. Thus, the total uptake of tannic acid by collagen is not increased, rather slightly lowered, while the uptake of the wattle and sulfited quebracho extracts is raised, although to a smaller degree than that of the irreversible fixation. In the work of Rao (15), the chroming of the hide powder to an extent of 7.6% Cr_2O_3, on the weight of the protein, followed by the removal of the ionic sulfate from the chromium sulfate–tanned hide powder by the pyridine method (16), gave the following figures for the increased binding of the tannins concerned in this context, on the basis of the corresponding fixation by straight hide powder, in percent: tannic acid, 12; myrobalans, 14; chestnut wood, 32; sulfited quebracho, 54; and wattle, 55. Any attempt to arrange the numerous vegetable tanning extracts in series as to the effect of the prechroming of the substrate on their binding is doomed to failure, since their degree of affinity for the chromed collagen varies considerably with the experimental conditions. Particularly, the pH value of the system has a marked effect on the fixation of the carboxylic tannins and nontannins by the chromium complexes with increasing pH of the systems.

THE REACTION POSSIBILITIES

It is not my intention to go into a detailed discussion of the numerous theoretical issues involved in this combination tannage, of which a few are mentioned in Kanagy's paper. These points have been comprehensively covered in earlier publications (8, 12). It suffices to refer to the series of papers recently published (8–12), particularly to ref. 8, which contains evidence for at least four different types of attachment of the irreversibly fixed wattle tannins by chromed collagen: (*a*) by the increased reactivity of the basic protein groups induced by the inactivation of the carboxylic groups of the collagen by the cationic chromium complexes, including data from the important paper by Burton and Vivian (7); (*b*) by displacement of sulfate ions electrostatically associated with the cationic protein groups (protein-

bound acid); (*c*) by displacement of the counterion sulfate, which is balancing the excess charges of the fixed chromium complexes, particularly in specimens of large content of chromium; and (*d*) by displacement of sulfato groups in the chromium complexes, or of aquo groups, resulting in the formation of chrome-vegetable compounds of great stability. In the latter instance, the formation of chelated complexes, especially by carboxylated phenols, as suggested by Kanagy (1), and earlier by Amos *et al.* (17), seems feasible.

The relative proportions of the various types of combination are known to vary according to the nature of the tannins, and particularly the phenolic nontannins and carboxylates generally, and most markedly with the pH of the system, to mention a few factors only. The distribution of the fixed tannins on the two main binding sites of the hide protein, the keto-imide groups and the basic protein groups, varies greatly for the different vegetable tanning extracts and with the experimental conditions (18). However, in no case has Kanagy offered binding experimental evidence against the concept given in the cited papers.

ESTIMATION OF THE UPTAKE OF VEGETABLE TANNING MATTER

Another important point in Kanagy's paper concerns the assessment of the amount of vegetable tanning matter fixed by the chromed collagen. In my notation the difference between 100 and the sum of collagen, ash (including Cr_2O_3), and the combined sulfate, on the fat- and moisture-free substance, represents the vegetable tanning material which has been incorporated with the substrate. The precision of the final figure of the combined tannin on hide-substance basis has in my experience been found to be about 1%. The sulfate is determined by oxidation with sodium peroxide (19), correcting for the sulfur content of the collagen, 0.2–0.3% S (due to methionine) on protein basis (0.6–0.9% SO_4). In some of Kanagy's tabulation sulfate determination was omitted, and factors were used for converting the percentage of Cr_2O_3 found on analysis to the "chrome complex" assumed to be present. Such a factor was first suggested by Kubelka (20). This item has been earlier discussed by Kanagy (21). The figure of Cr_2O_3 found should be multiplied by 2.73, according to Kubelka's proposal, in order to account for the composition of the "chrome complex" fixed in the leather, including chromium, hydroxy or Ol-groups, aquo groups, and the anion of the chromium salt used (generally sulfate). Kanagy has suggested other factors and modes of correction (1, 21). The Kubelka conversion factor is not applicable to vegetable-retanned chrome leather generally, nor to straight chrome leather. The last-mentioned case is unequivocally demonstrated by the data in Table I of Kanagy's paper (1). In the present author's opinion, the conversion factor is *not* applicable in any case.

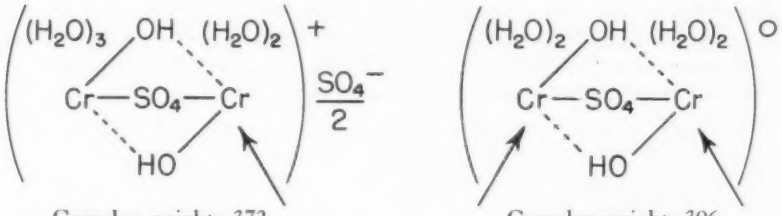
Kanagy's data prove this conclusively for the two specimens of chromed hide substance exemplified. Thus, the sum of protein, Cr_2O_3, and total sulfate stated as H_2SO_4, is 98.5% of the total dry substance. By an oversight Kanagy has not corrected his figures of total sulfur for the protein sulfur (0.6% as SO_4). However, since the soluble ash content is not included (as Na_2SO_4), which in corresponding cases generally is in the range 0.2–0.6%, the two omissions will tend to cancel each other. Taking an example from Kanagy's paper, with the data on the completely neutralized leather of Tannage 1 (No. 4), free from sulfate, the figures add up to 98.5% after due correction for protein sulfur (as SO_4). If Kubelka's factor is applied, the "chromium complex" for this sample would represent 5.17×2.73, or 14.1% of the dry weight. Then, the figures for hide substance and chrome complex would add up to 93.3 + 14.1, or *107.4*%.

According to my own experience, the figures of protein, ash (including Cr_2O_3), and total sulfate account for 98.5–99.0% of the dry substance as a rule. Thus, the data in Table I (8), covering the complete analysis of chromium sulfate–tanned hide powder, with Cr_2O_3 contents from 2.0% to 14.3% on protein basis (pyridine-treated), give an average of 98.6%. The soluble ash was within the limits: 0.1–0.4%. For the chromium chloride–tanned hide powder, five specimens in all, with Cr_2O_3 contents from 2.2% to 10.9% on protein basis, the sum of ash (Cr_2O_3), collagen, and combined Cl, was 98.6, 98.9, (97.2), 99.8, and 99.7, averaging 99.2% of the weight of the dry substance (Table I [9]). For the specimens of the chromium chloride tannage given in Table III of the cited paper, the figures from the record of the analysis add up to the average percentage of 99.3.

The only doubtful point in such assessments is the tenacity of the aquo groups in the fixed chromium complexes. Apparently, on the drying of the sample for analysis, at 105°C. for some 12 hours, at the most two aquo groups will resist the drying. One aquo group present in the fixed chromium complex of the general composition $Cr_2(OH)_2SO_4$ would add 12% of the Cr_2O_3 figure, and two aquo groups 24% accordingly. In the data presented, only one aquo group can be accomodated. It appears to this author that variations of the factor for converting N into hide substance (5.56 for his own data cited) well can account for the small deficit found (1%), which is of the order of the accuracy of the analytical technique. The use of the N-factor of 5.62, officially sanctioned for leather analysis and for hide powder (17.8% N), on lightly limed hide substance, both bovine pelt and hide powder (Lyon), may introduce an appreciably greater error than the factor just discussed. Hence, it is imperative to make a rule of estimating the N content of the ash- and fat-free dry substance of the collagen substrate to be used (22), particularly so when ascertaining figures indirectly from the hide substance value, such as the degree of the vegetable tannage, straight, and combined.

THE FAILURE OF A CONSTANT FACTOR

It should be obvious from the presented critical survey that the suggestion of applying a constant factor, such as Kubelka's factor of 2.73 × Cr_2O_3 in the analysis of chrome and chrome–combination-tanned leather, to obtain the "chrome complex" in order to account for substances in the chromium complexes not determinable by the ordinary analytical methods, is incongruous. However, it should be of interest to examine the possible use of such a factor for approximating the value of the sulfato-chromium complexes present in wet, lightly washed chrome leather immediately after tanning. The over-all acidity of the "chrome-collagen-compound", i.e., the sulfato-chromium complex + ionically associated sulfate (protein-bound acid and counterions), is generally about 60. Assume that the chrome leather contained 3.0 meq. Cr and 1.8 meq. combined SO_4, on the weight of the collagen. Of the sulfate, an amount of 0.9 meq. was held in direct association with chromium in the complex (sulfato groups), according to the analysis of the pyridine-treated specimens (16). The sulfate present as counterions on the fixed chromium complexes amounts to 0.5 meq. (23). That leaves 0.4 meq. SO_4 ions as protein-bound acid. These data indicate the presence of chromium complexes in the fully hydrated chrome leather (wet) of two general types: uni- and bipointly attached to the collagen, in about equal amounts (judging from the value of the counterion sulfate [24]):



Complex weight: 372
Unipoint combination

Complex weight: 306
Bipoint combination

⟶ = COO − groups of collagen

Thus, the factor for converting Cr_2O_3 into the "chrome complex" should be: $\frac{339}{152} = 2.2$ for the *wet* leather. On drying it at 105°C. for analysis, the complexes will probably lose four H_2O at least. The factor would then be 1.8. In this instance, the "chrome complex" would account for 13.7% of the dry weight. From the direct analysis for Cr_2O_3 and combined sulfate the figure would be 13.6% (7.6 + 6.0). This excellent agreement of the values may be conceived as a justification of the suggested type formula for the "chromium complex."

Turning to the vegetable-retanned chromium sulfate–tanned hide substance, the acidity of the sulfato-chromium complex generally is lower than 33%—values in the range 18–20% being common in heavy retanned leather (2, 12). Then the conversion factor would be of the order of 1.5–1.6. On the other hand, for a chrome-vegetable type of leather with 5.0% Cr_2O_3, on protein basis, the Kubelka factor would indicate 13.7% of the dry substance to be in the form of the "chrome complex", while actually it amounts to 8%. Thus the error is 6% on the dry weight and considerably more on hide-substance basis. Obviously, in the example given, any vegetable tanning material which has penetrated into the chromium complex is not included in the value for the "chrome complex", since that fraction should be accounted for as irreversibly fixed vegetable tanning matter (12).

In the vegetable-retanned chromium chloride–tanned collagen, *no* anions are present in the combined state (9). The analytically obtained Cr_2O_3 is practically identical with the "chrome complex" in the combination-tanned leather. Hence, the application of the 2.73 factor will give highly erratic figures for the uptake of vegetable extracts by this type of chrome leather. As is well known, the composition of the chrome complexes of vegetable-retanned chrome leather varies widely, which fact would in itself invalidate the idea of using a standard conversion factor.

DEDUCED FORMULAE

Table II (1) contains a column with an alternative for assessing the degree of the vegetable tannage by "difference", presupposing that the original chromed stock remains unaltered and intact as to composition upon its heavy retannage with sulfited quebracho extract. As pointed out by Kanagy, this is purely a construction. Column No. 2 of Table II in ref. 1 represents the mode of calculation used successfully in the assessment of composition of the straight chrome leather (Table I [1]), which relies upon the analytically ascertained figures for Cr_2O_3, total sulfate, and collagen.

Actually, this is the standard method introduced in the 1927 paper (2) with due correction for an apparent misprint in Kanagy's formula, as already pointed out. It appears to me that there is no need for such formulas, since the old method shows remarkably close agreement with the formula of Kanagy's preferred choice. According to method No. 2 (1): % tannin = $100 - \left(A + \frac{0.5}{100} A\right)$ where A is defined as % (hide substance + Cr_2O_3 = H_2SO_4). In this definition of A, the "equal" sign should probably have been a "plus" sign. Applying this corrected formula to the data on the wattle-retanned specimens of chromium sulfate–tanned hide powder in Table II in my recent paper (8), the figures for fixed tannin on hide-substance basis check exactly the figures given in the table, obtained by analysis for total ash (including

Cr_2O_3), total sulfate, and hide substance in six of the seven cases. For the remaining specimen (No. 7), the values are 87% and 89% for the deduced and analytically obtained data, respectively. Applying the factor of 2.73 to the Cr_2O_3 - figures of the same specimens (Table II [8]), the error of the amount of fixed tannin grows with the chrome content of the chromed protein. Thus, for the three most extensively retanned specimens, with percent fixed tannin on the weight of collagen of 78, 84, and 87, which values were obtained by direct analysis, the use of the 2.73 factor gives the figures 66, 69, and 70. In these instances, the deduced figures are 15–20% too low, based on the directly obtained values.

In view of these facts, demonstrating the close agreement between the data obtained by the formula of Kanagy and by the method introduced in the present author's first contribution to this problem 35 years ago and consistently used up to the present time, it is difficult to understand Kanagy's statement (p. 254 [1]): "Errors in the determination of vegetable tannins in retanned leather in previous work have undoubtedly led to overestimation of the amount of vegetable tannins combined." Such an unjustified statement conveys insufficient familiarity of that author with the published records on the chrome-vegetable combination tannage.

ACKNOWLEDGMENT

The author is pleased to acknowledge most gratefully the financial support of the investigations in this field, which have been carried out for a number of years, by generous grants from *The Swedish Technical Research Council.*

REFERENCES

1. Kanagy, J. R. *JALCA*, **56**, 252 (1961).
2. Gustavson, K. H. *JALCA*, **22**, 125 (1927).
3. Page, R. O., and Holland, H. C. *JALCA*, **27**, 163, 432 (1932).
4. Gustavson, K. H. "Die Kombinationsgerbung" in Grassmann's *Handbuch der Gerbereichemie* (Vienna: Springer, 1939) II/2, 580–94.
5. van Vlimmeren, P. J. *J. Soc. Leather Trades Chem.*, **31**, 259 (1947).
6. Gustavson, K. H. *Ibid*, **33**, 68 (1949).
7. Burton, D., and Vivian, G. W. "Festschrift Wiener Versuchsanstalt" Oester. Leder-Z. Festnummer, 1954, C 21.
8. Gustavson, K. H. *J. Soc. Leather Trades Chem.*, **42**, 149 (1958).
9. ———. *Ibid.*, 191.
10. ———. *Ibid.*, 312.
11. ———. *Ibid.*, 368.
12. ———. *The Chemistry of Tanning Processes* (New York; Academic Press, 1956).
13. Page, R. O. *JALCA*, **23**, 495 (1928).
14. Otin, C. O., and Alexa, G. *J. Int. Soc. Leather Trades Chem*, **18**, 418 (1934).
15. Rao, P. H. *JALCA*, **49**, 719 (1954).
16. Gustavson, K. H. *JALCA*, **22**, 60 (1927).

17. Amos, G. L., Thompson, G. W., and Tolliday, J. D. *J. Soc. Leather Trades Chem.*, **42,** 232 (1958).
18. See ref. 12, pp. 160–75; Gustavson, K. H., *Svensk Kem.Tidskr.*, **53,** 324 (1941).
19. Rao, P. H. *JALCA*, **49,** 755 (1954). See originally: Gustavson, K. H., *Ingeniörsvetenskaps-Akademiens Handlingar*, No. 177, 1944, p. 47.
20. Kubelka, V. *Tech. Hlidka Koz.*, **23,** 91 (1948); abst. *JALCA*, **44,** 45 (1949).
21. Kanagy, J. R. *JALCA*, **52,** 142 (1957).
22. Bowes, J. H., and Kenten, R. H. *J. Soc. Leather Trades Chem.*, **32,** 308 (1948).
23. Gustavson, K. H., *JALCA*, **21,** 559 (1926).
24. ———. *JALCA*, **48,** 559 (1953). See also ref. 12, pp. 124–34.

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The fragmentary evidence from earlier centuries shows us that parchment was then too made of goat or sheep skins, depilated with urine, perhaps treated with lye of wood-ashes and the hair scraped off subsequently. The parchment was then stretched in a frame and treated with flour and salt or with lime, smoothened with pumice stone on the flesh side and coated with chalk. Very strong qualities were made from the skins of hogs, asses, calves and even wolves. Parchment was not only used for writing but it was used for drums, sinews of instruments, etc. Very thin parchment was produced too for Pliny tells us that "Cicero records that a parchment copy of Homer's poem the Iliad was enclosed in a nutshell". —R. J. Forbes. "Leather in Antiquity" in *Studies in Ancient Technology*, Vol. V (Leiden, the Netherlands: E. J. Brill, 1957).

Caesar tells us that the Celts were clever leather-workers. The Veneti used sails of "aluta" (soft, flexible leather) which is usually identified with alum-dressed leather. He also observes that the natives of Britain covered their boats with "corium" indicating a firmer kind of leather, possibly ox-hide. Indeed the word "coracle" denoting such vessels is derived from the term "corium".—R. J. Forbes. "Leather in Antiquity" in *Studies in Ancient Technology*, Vol. V (Leiden, the Netherlands: E. J. Brill, 1957).

LIFE LINES

Brief Biographies of Our Contributors

DR. JOANE H. BOWES received her B.Sc. degree at Bedford College in the University of London in 1933 and went on to do research on the chemical composition of teeth for which she was awarded the degree of Ph.D. She joined the B.L.M.R.A. staff in 1936 and has been chiefly concerned with work on formaldehyde and mineral tannages, liming, and pickling. Her chief interest has been the chemical composition and properties of the skin proteins, and for this work she received the D.Sc. of London University in 1958.

DR. K. H. GUSTAVSON is too well known to require an extended biographical note. His chief interest is chrome tanning, but he has made numerous and important contributions to nearly every facet of leather manufacture and is universally recognized as one of the foremost leather chemists of our time. After some ten years in the United States, during which he contributed frequently to this *Journal* as an active member of ALCA, he returned to Sweden in the mid-30's. He is now Director of the Tanning Research Institute in Stockholm.

A. S. RAISTRICK was awarded the Associateship of the Royal College of Science and the B.Sc. degree at Imperial College of Science and Technology, London, in 1957. On graduating he was appointed B.L.M.R.A. Research Fellow in the Department of Leather Industries, Leeds University. Since 1958 he has been working at B.L.M.R.A. on chemical aspects of the deterioration of leather and collagen.

* * * *

Life Lines of the authors of "On the Stability of Lime Suspensions", a paper published in last month's Journal, *were received too late for inclusion in that issue and are given below.*

D. JANNAKOUDAKIS received his Bachelor's degree in chemistry from the University of Thessaloniki, Greece, in 1951 with high honors. He served as a laboratory assistant of physical chemistry at the University from 1952 to 1960, earning his Ph.D. in 1958 and an appointment as assistant professor this year at the same university. During the academic year 1960-61 he received a research scholarship from the University of Hamburg, Germany, where he did research work under Prof. L. Holleck and became a member of the Bunsengesellschaft für Physikalische Chemie. His special research interests include conductivity, photochemistry, precipitation, and polarography.

B. STRATES, born in Greece in 1927, graduated from Corfu High School in 1946 with high honors. He received his Bachelor's degree in chemistry from Clark University, Worcester, Mass., in 1953, after serving with the Greek Army. In 1956 he was granted an M.Sc. in Pharmacology by the University of Rochester where he served as a research fellow under Prof. W. F. Neuman. Since 1958 he has been an assistant professor (oberassistent) of Pharmaceutical Chemistry at the University of Thessaloniki, Greece, where his fields of special interest are precipitation, solubility, stability of pharmaceutical suspensions, and drug control.

G. VASSILIKIOTIS, born in Russia in 1931, received his Bachelor's degree in chemistry from the University of Thessaloniki, Greece, in 1955 with high honors. After serving with the Greek Army, he was appointed laboratory assistant of Pharmaceutical Chemistry at the University of Thessaloniki in 1958. In 1960 he received a scholarship from the University of Wisconsin, where he is studying for his Ph.D. He is particularly interested in precipitation.

E. VOYATZAKIS, born in Crete in 1907, received his Bachelor's degree in chemistry from the University of Athens in 1928. Following completion of his service duties, he was appointed laboratory assistant of General Chemistry at the University of Thessaloniki (1930–39), earning his Ph.D. there in 1936. During the academic year 1938–39 he received a research scholarship from the University of Paris, where he did research work under Prof. Maurice Curie. In 1939 he returned to the faculty of Thessaloniki where he is now Associate Professor. His special research interests are complex compounds, solubility, conductivity, photochemistry, and precipitation.

Unfortunately no Greek tannery has been excavated but we have the remains of such tanneries of Roman date in Pompeii, Bonn, Wiesbaden and Mainz. In the Pompeii tannery one room, the former atrium of a dwelling house (8.50 by 9.00 m., the middle roof supported by a pillar) was used for the mechanical treatment of the hides, which arrived in bundles of ten. It was separated by a low wall from a back room, which had 15 round pits (1.25–1.60 m. in diameter and about 1.50 m. deep), lined with stucco, in the walls of which there were two steps to allow the workmen to descend into these pits and clean them out. These pits served for vegetable tanning. These pits were arranged in sets of four. Enclosed by two pairs of these pits there were rectangular pits, some 0.50 m. deep, probably originally lined with timber and used for mineral tanning. On each side of these rectangular pits there was a pottery container for the storage of fresh tanning solution or tanning agents. An open porticus at the back of the house was used to prepare the fermenting solutions and the tanning infusions. Here the liquids flowed from a masonry tank partly into a low basin and partly through an open conduit along the wall into three large pottery vessels partly buried in the floor. In the first room were found many instruments, which differed little from those now in use. There were the blunt-edged concave scrapers, the currier's knife, the half-moon knife, awls (or rather steel edging tools?) and other tools.—R. J. Forbes. "Leather in Antiquity" in *Studies in Ancient Technology*, Vol. V (Leiden, the Netherlands: E. J. Brill, 1957).

ALCA NEWS

Proceedings, Reports, Notices, and News

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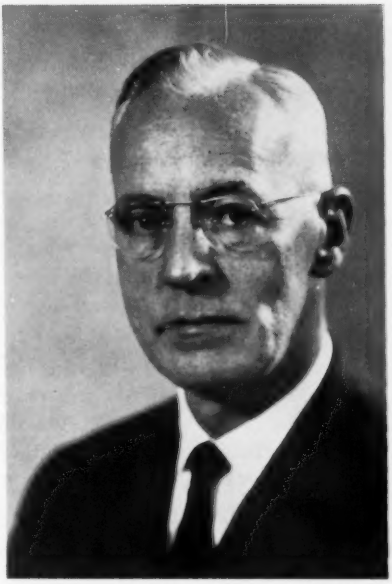
ALSOP AWARD

Dr. Wallace Windus was presented the Alsop Award at the I.U.L.C.S. Meeting in Washington August 20–25. The award was made by Dr. H. G. Turley, Chairman of the ALCA Awards Committee, who introduced Dr. Windus as follows:

"We present to you a member who has brought great credit to our Association, Dr. Wallace Windus, for the 1961 Alsop Award.

"In school and later in college Dr. Windus showed great aptitude for chemistry, and at the end of his academic career he received the Ph.D. degree in organic chemistry. In this research he pioneered with an important synthesis of the amino acid methyionine. He also participated in the early work on isolation of the then unknown amino acid threonine.



U.S.D.A. Photo by M. C. Audsley

DR. WALLACE WINDUS

"After graduation, he joined the Rohm & Haas Company and for 13 years worked in the Leather Chemicals Department, first in research and later in sales. During the course of his research in leather Dr. Windus established some important principles, particularly with respect to the theories of unhairing or depilation. He found that the class of simple organic thiol compounds had depilating properties as great as those of sodium sulfide. He offered the first rigid proof of the reduction theory of unhairing by demonstrating the quantitative oxidation of benzyl mercaptan to benzyl disulfide during the unhairing reactions. I think this is still the only example of a firm proof of the reduction theory of unhairing. Dr. Windus also spent considerable time with developing and perfecting the enzyme-unhairing process—the Arazym process—for the manufacture of glazed kid.

"Later, he joined the John R. Evans organization and while there invented and perfected a new type of tannage based on the resorcinol-formaldehyde tanning *in situ*. This gave very satisfactory leather used for special purposes,

among which might be mentioned the Arctic mukluks for the United States Air Force.

"Later, Dr. Windus went into the sales field with Tanimex Company, during which time he worked also in the manufacture of syntans.

"Windus joined the staff of the Eastern Utilization Research and Development Division of the U. S. Department of Agriculture in the Hides and Leather Laboratory. While here he has contributed to the dialdehyde starch–tanning development, glutaraldehyde-tanning development, and an enzyme-unhairing project.

"As Editor he has steered the *Journal of the American Leather Chemists Association* for the past three years and will shortly retire from this position. It is generally thought that the *Journal* has been in capable hands, as I think you will agree from the appearance and contents of our present August Conference number.

"On the personal side, Windus has two hobbies that I know of. He collects modern paintings. (For a practical leather chemist it is surprising to see that he favors the abstract painters—perhaps this is a sublimation from the complexities of leather making.) He also is a successful amateur gardener, specializing in lilies, and has won many awards in national exhibitions.

"The Awards Committee was unanimous in its choice of Dr. Wallace Windus as the recipient of the Alsop Award."

Dr. Windus responded:

"I am highly honored to be the 1961 recipient of the Alsop Award. This comes as a distinct and pleasant surprise. I do not feel that this honor should be mine alone. I am indebted to many chemists and tanners for inspiration and help. I have been fortunate in working in several capacities and in having the opportunity to associate closely with tanners. Familiarity with an industry is bound to influence one's thinking about research. To me, this is very desirable. The Utilization Research Laboratories of the Department of Agriculture also provide substantial opportunities for both basic and applied research.

"Dr. Turley has referred to our *Journal*. It has been close to my heart. I feel that it is a distinguished industry journal. I should like to make a last appeal, before my term as editor expires, for more applied research papers from industry in order to provide a better scientific balance.

"I am deeply grateful for the honor bestowed upon me this evening."

WINHEIM AWARD

During the Seventh Biennial I.U.L.C.S. Meeting in Washington August 20–25 the Winheim Award of the ALCA was presented to Theodore B. Brother by Dr. H. G. Turley, Chairman of the Awards Committee, with the following words:

"The Awards Committee chose for the presentation of the Winheim Award Mr. Theodore B. Brother. Mr. Brother is a product of Massachusetts, our New England Leather State. He was born in Boston and educated in the Boston Public Latin School and the Roxbury Memorial High School. At present he is pursuing research in leather problems at the Lowell Technological Institute.

Photo courtesy of The Leather Manufacturer

Lt. Theodore B. Brother, U.S.A.F., receives the Winheim Award from Dr. Reuben G. Henrich, ALCA president.

"Mr. Brother was chosen for the Winheim Award for his fine work on the question of the action of the enzymes on the mucopolysaccharides of steerhide. His preliminary report on this work was published in the eminent scientific periodical *Nature* in 1960, under the title of 'Liberation of Hexuronic Acid, Hexosamine, and Hydroxyproline from Steerhide by Stem Bromelain'. This work is of significant importance for our understanding of the enzyme method of unhairing.

"We recommend Mr. Brother as a worthy recipient of the Winheim Award. He is serving his country as a First Lieutenant in the U.S. Air Force, stationed at Lincoln, Nebraska, but was able to obtain leave to be present for this ceremony.

"With this award go our best wishes for his future career in the Air Force and the hope that in less troubled times he will return to the field of leather research."

Mr. Brother received the Winheim Award graciously, with a few words of appreciation.

Photo courtesy of Leather and Shoes

DOMINIC MEO, JR.

The success of the Seventh Biennial I.U.L.C.S. Conference was due in large measure to the untiring efforts of the general chairman, dynamic Dominic Meo, Jr., Salem Oil & Grease Company.

Photo courtesy of The Leather Manufacturer

***JALCA* EDITORIAL BOARD**

ALCA officers pose with members of the *Journal's* editorial staff during the I.U.L.C.S. meeting last June. (*L. to R.*) Dr. H. G. Turley; Dr. Wallace Windus, Editor; Dr. J. R. Kanagy; Dr. Fred O'Flaherty, Secretary-Treasurer; Dr. L. P. Witnauer; Dr. Stephen Shivas; Dr. John H. Highberger; and Dr. Reuben Henrich, President.

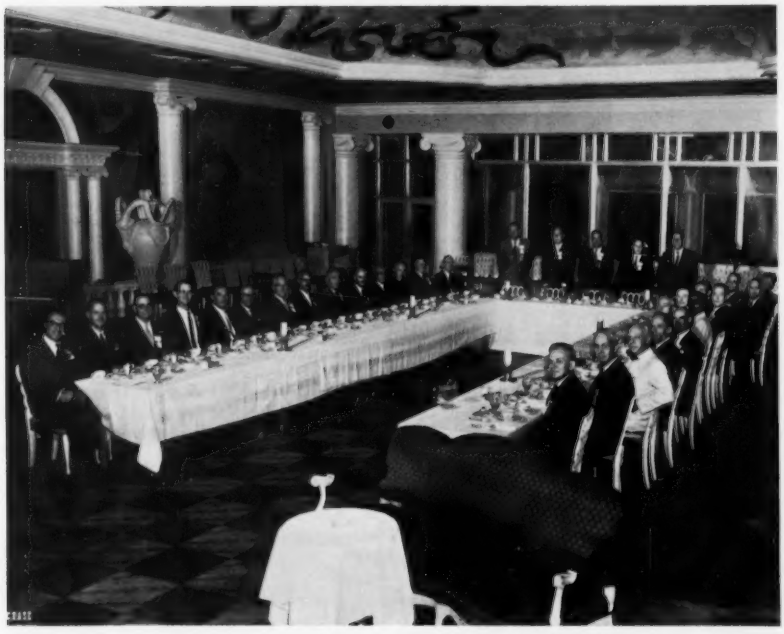


Photo courtesy of The Leather Manufacturer

TOP LEATHER FIGURES AT I.U.L.C.S. MEETING

(*L. to R.*) Dr. Villa, Director, Research Institute for Leather Industries, Lyons, France; S. C. Walker, Collis Leather Co., Canada; E. R. Thorstensen, Past President of ALCA; Mieth Maeser, Past President of ALCA; John Ivany, A. C. Lawrence Leather Co.; Joseph Knoepfler, Supt., Cortume Carioca, Rio de Janeiro, Brazil; Elcanna Peterson, Supt., Geilich Tanning Co., U.S.A.; E. L. Jensen, Technical Institute, Copenhagen, Denmark; H. Y. Miller, Seton Leather Co., U.S.A.: Prof. Alan Ward, Prof. of Leather Science, University of Leeds, Leeds, England; Dr. John Highberger, United Shoe Machinery Corp., U.S.A.; Dr. Ing. Hans Herfeld, Director of West Germany Leather Institute; Dr. Ronald Mitton, British Leather Manufacturers Research Association; Dr. Fred O'Flaherty, Director, Tanners' Council of America Research Laboratory; Dr. Reuben Henrich, President of ALCA; Dr. Prof. Wolfgang Grassmann, President, International Union of Leather Chemists Societies, and Director of Max Planck Institute, Germany; Dominic Meo, Salem Oil & Grease Co., Salem, Mass., and General Chairman of the Washington Meeting; Ir P. J. van Vlimmeren, President Elect of I.U.L.C.S., Holland; Dr. Robert Stubbings; Director of Leather Technology, Milwaukee School of Engineering, U.S.A.; Dr. E. Baumann, Research Director of Bally's Shoes, Switzerland; Marcel Rivière, Vice President of French Chemists Association for Leather, and John Arthur Wilson Memorial Lecturer; Dr. H. G. Turley, Past President of ALCA and I.U.L.C.S., Rohm & Haas Co., U.S.A.; Irving Glass, Executive Vice President, Tanners' Council of America; Baron Ludwig C. Heyl, Jr., Heyl's Leather Works, Germany; Dr. Joseph Naghski, Chief, Eastern Regional Bureau, USDA: Dr. Y. Nayudamma, Director, Central Leather Research Institute, India; Robert Weldon, Radel Leather Co., U.S.A.; John M. Harrison, Walker & Martin Tannery, England; Wendell Morris, Endicott-Johnson Corp., U.S.A.; Dr. Ernesto Mezei, Buenos Aires, founder of the Argentine Leather Chemists Society; Dr. Wallace Windus, USDA, and winner of the 1961 ALSOP award; and Dr. Joseph Kanagy, National Bureau of Standards, U.S.A.

Photo courtesy of The Leather Manufacturer

EXECUTIVE COMMITTEE OF THE I.U.L.C.S.

Meeting during the Seventh Biennial I.U.L.C.S. Conference in Washington, D. C. were (*L. to R.*): Dr. E. Baumann, Bally Shoe Factories, Switzerland; Mieth Maeser, United Shoe Machinery Corp., Beverly, Mass.; Prof. Alan G. Ward, Procter Dept. of Food & Leather Science, University of Leeds, England; J. Marcus Harrison, Walker & Martin Tannery, England; Dr. Prof. W. Grassmann, Max Planck Institute, Munchen, Germany; and Ir P. J. van Vlimmeren, Leather Research Institute, Holland.

U.S.D.A. Photo

WORLD AUTHORITIES ON LEATHER VISIT USDA LABORATORY

Following the meeting of the International Union of Leather Chemists Societies in Washington, D. C., a number of the conferees visited the Hides and Leather Laboratory of the U. S. Department of Agriculture's Eastern Utilization Research and Development Division, near Philadelphia, on August 28. Dr. Joseph Naghski is chief of this laboratory; Dr. Edward F. Mellon heads investigations of hide composition; Dr. Edward M. Filachione heads investigations of chemical modifications for hides; and Dr. Wallace Windus heads processing investigations. Group picture taken during the visit shows (left to right, front row) Georges Blancher, Société Rapidase, Seclin Nord, France; Merrill Budden, Messrs. Whitmore's Edenbridge, Ltd., Kent, England; H. E. Herman, Gorey Leather Co., County Wexford, Ireland; L. Villa, Institut de Recherches pour les Industries du Cuir, Lyons, France; Dr. Naghski; Dr. Windus; Dr. R. Lasserre, Institut de Recherches pour les Industries du Cuir; Charles Alabouvette, L'Association Française des Chimistes des Industries du Cuir, Paris; Henri Lutun, Société Minoc, Paris; (back row, left to right) Dr. Mellon; Michel Giroflier, Centre Technique du Cuir, Lyons, France; Josué Monteiro, Fabrica Portuense de Curtumes, Ltda., Porto, Portugal; R. Durand-Ayme, Institut de Recherches pour les Industries du Cuir; and Dr. Filachione.

COUNCIL MEETING MINUTES

Shoreham Hotel
Washington, D. C.
August 20, 1961

The meeting was called to order by President Henrich at 9:10 P.M. Present were Messrs. Tetreault, Miller, Wederbrand, and O'Flaherty.

The minutes of the meeting of June 8 were given final approval as published.

Mr. Wederbrand reported that as of this date the Association was operating within the budget.

There was no old business.

The following members were elected to active membership:

James C. Perkins, Jr.
Claude J. Schmidle
Edward A. Strauch

President Henrich appointed the following tellers for counting the ballots at a time after noon on Tuesday, August 22:

Wm. T. Roddy, *Chairman*
E. Stein
R. Eddy

There being no further business, the meeting adjourned at 10:00 P.M.

Respectfully submitted,
FRED O'FLAHERTY
Secretary

August 24, 1961

The meeting was called to order by President Henrich at 8:40 P.M. Present were Messrs. Stubbings, H. Y. Miller, Benrud, Filachione, Grota, Wederbrand, Meo, and O'Flaherty. Dr. Lollar was absent. Dr. Henrich welcomed the new members, Messrs. Benrud, Filachione, and Grota, to Council.

Dr. Stubbings, reporting for the Technical Committees, advised that they have discontinued further work until the ALCA-ASTM Joint Committee has completed its review of the methods. William Roddy has accepted the chairmanship on the International Commission of Chemical Properties of

Leather. The other commission representatives will be the chairmen of the ALCA corresponding committees. Council discussed voting on international methods. Dr. Stubbings made a motion that any method of the international methods to be approved must be approved by the ALCA Council before being approved by the Association delegates. The motion was seconded by Mr. Miller and approved.

Dr. Windus, Editor-in-Chief, reported he has a good supply of papers for publication on hand.

Mr. Meo, Convention Chairman, advised that the technical program of this meeting was up to standard. The expenses are within the proposed estimates, and income from registration is higher than expected. Council decided to await the final accounting of the convention funds before making any distribution of the excess, if there be any. Mrs. Henrich reported that the special activities planned by the Ladies' Committee were self-supporting.

Mr. Wederbrand, Ways and Means Chairman, reported the Association's finances are in satisfactory condition. Printing expenses are high due to printing Supplements #7 and #8. Mr. Wederbrand requested Council to help increase the advertising revenue of the *Journal.*

Dr. Henrich advised Council of the memorial being established in honor of Dr. Stiasny. Mr. Miller made a motion to table the matter for the present. Mr. Benrud seconded the motion and Council approved.

The committee to select the new Editor-in-Chief, Messrs. Roddy, Miller, and Somerville, recommended Dr. Joseph Kanagy. Dr. Stubbings moved that Council accept the committee's recommendation. Dr. Filachione seconded this motion, and Council approved.

Dr. O'Flaherty advised Council he had looked into reinvesting the Association's funds but was advised to keep the funds invested in government bonds as they are now, in view of the Association being a nonprofit organization.

Dr. Henrich, with Council's approval, appointed the following three committees:

1962 Awards Committee, to recommend a candidate for the Alsop Award—Dr. W. Windus, Chairman, and Drs. Somerville and Panepinto.

1962 Nominating Committee, to select candidates for President-Elect and two Council Members—Mr. Tetreault, Chairman, and Messrs. C. Morrison and L. Meyers.

John A. Wilson Memorial Speaker for 1963—Messrs. H. Y. Miller, Chairman, with Dr. Kanagy and Mr. Meo.

Mr. Wederbrand reported to Council on future meeting sites. He presented a résumé on Whiteface Inn on Lake Placid and on the New Ocean House at Swampscott. He also passed along the suggestions of Wentworth-By-The-Sea, and possibly of meeting in the Ashville, North Carolina, area. Thought was given to meeting possibly in Canada and also Atlantic City, where we were to have met this year at the Chalfonte-Haddon Hall Hotels. Mr. Miller moved that the Association meet, if suitable dates can be arranged, at the Grand Hotel on Mackinac Island in 1965. The motion was seconded by Mr. Benrud and approved. Mr. Wederbrand was requested to contact the Grand Hotel for dates in 1965 and the Chalfonte-Haddon Hall Hotels for dates in 1966. A mail vote can be taken on these dates.

Mr. Wederbrand suggested that in order to obtain the meeting dates the Association wants, Council should consider establishing a regular routine of going to the same two hotels in the East and one in the West. Council decided on the Grand Hotel on Mackinac Island as the hotel in the West and Lake Placid Club as one of the hotels in the East; the third hotel site will be rotated until a suitable place is found. Mr. Wederbrand will advise Whiteface Inn and the New Ocean House of Council's decision.

Mr. Fred Klimpl has accepted the chairmanship of the 1962 and 1963 Conventions.

Council requested the President to appoint a chairman, from persons recommended, to consider presenting a panel discussion on fatliquoring of leather at the next annual meeting. If such a discussion is feasible, all oil suppliers will be invited to participate.

Council wishes to continue having exhibit booths at the annual meeting. The present cost of $100.00 per booth will continue next year.

The following persons were elected to active membership:

John Mirza
Alberto Simoncini

The next meeting of Council will be held in Boston, on Wednesday, November 15.

There being no further business, the meeting was adjourned at 10:30 P.M.

Respectfully submitted,
FRED O'FLAHERTY
Secretary

REPORT OF THE HIDE POWDER COMMITTEE

A sample of hide powder furnished by Mr. Frank F. Marshall, Ridgway, Pa., and representing a batch designated as Lot No. 29, has been tested by the ALCA Hide Powder Committee. Average values found by the Committee members in certain comparative tests with ALCA Standard Hide Powder Lot No. 28 and the proposed Lot No. 29 were as follows:

	Hide Powder Lot	
	No. 28	No. 29
Date of testing	Sept. 1959	Sept. 1959
Water soluble content, Blank test residue (grams)	0.0039	0.0036
Ash, %	0.16	0.18
pH	5.22	5.28
Nontannin, grand average, %	20.19	20.05

The Committee has approved the new hide powder. Mr. Frank Marshall was authorized to issue the hide powder represented by the sample as ALCA Official American Standard Hide Powder Lot No. 29.

A. N. KAY — F. L. COLLINS
J. F. WAGONER — F. F. MARSHALL*
G. W. SCHULTZ — F. P. LUVISI, *Chairman*

*Participated in the testing but not in the approval of the hide powder as official.

DIRECTORY CHANGES

NEW MEMBERS

Frank J. Badik, 128 Church Road, Elkins Park 17, Pennsylvania. Wm. Amer Company, 215 Willow Street, Philadelphia 23, Pennsylvania.

Leo D. Kahn, 8121 Eastern Avenue, Philadelphia 18, Pennsylvania. U. S. Dept. of Agriculture, 600 East Mermaid Lane, Philadelphia 18, Pennsylvania.

J. H. Lubbehusen, 15 Brown Ct., Midland, Michigan. Dow Corning Corporation, Midland, Michigan.

Tadasumi Masuda, Japan Leather Company, Ltd., Adachi, P. O. Box No. 3, Tokyo, Japan.

John Mirza, 2303 E. Bristol Street, Elkhart, Indiana. Miles Chemical Company, 1127 Myrtle Street, Elkart, Indiana.

Richard Neumann, 1344 East 19 Street, Brooklyn, New York. Richard Neumann Tannery, Inc., 91 Colden Street, Newark 4, New Jersey.

James C. Perkins, Jr., 2934 Rollingwood Road, Petersburg, Virginia. QM R&E Field Evaluation Agency, Fort Lee, Virginia.

Pierre Saint-Priest, 312 Woodland Avenue, Avon-by-the-Sea, New Jersey. Goldsmith Leather Company, 121 Paris Street, Newark 5, New Jersey.

Claude J. Schmidle, 1 West Harris Avenue, Moorestown, New Jersey. Rohm & Haas Company, 5000 Richmond Street, Philadelphia, Pennsylvania.

Alberto Simoncini, Via Mergellina 8h, Napoli, Italy.

Stuart A. Spaulding, 175 Cutler Road, S. Hamilton, Massachusetts. A. C. Lawrence Leather Company, Peabody, Massachusetts.

Edward A. Strauch, 15205 Marilyn Drive, Elm Grove, Wisconsin. Diamond Alkali Company, 20 N. Wacker Drive, Chicago 6, Illinois.

CHANGES OF ADDRESS

George Alt, 404 Crestwood Court, Endicott, New York.

Ross Barbour, c/o I. Weissman, 20 W. 47th Street, New York 19, New York.

Raymond N. Berg, 6402 West Cleveland Avenue, Milwaukee 14, Wisconsin.

Jose Berliavsky-Urow, Suelas y Pieles Torreon, S.A., Avenue Victoria #1510, Ote. Torreon, Coahuila, Mexico.

Harry C. Berndt, 388 Lakeshore Road, Toronto 14, Ontario, Canada.

George A. Butz, 2710 Columbia Drive, Endicott, New York.

J. Thomas Chain, R.D. #6, Chardon, Ohio.

Ralph E. Colby, 207 Indiana Avenue, Mt. Dora, Florida.

Ell Dee Compton, Maumee Chemical Company, 1310 Expressway Drive, Toledo 8, Ohio.

Leo P. Devarenne, Ciba Company, Inc., 7535 Lincoln Avenue, Skokie, Illinois.

Eduardo V. Diharce, 1041 Ravine Road, Apt. #3, Oshawa, Ontario, Canada.

Caspar Drueding, The Wyncote House, Wyncote, Pennsylvania.

Frank J. Drueding, 1635 Terrace Drive, Maple Glen, Pennsylvania.

Charles A. Eisenfelder, Jr., 11 Ainslie Court, East Brunswick, New Jersey.

Theodore Feldman, Bay State Oil Products, Inc., 2 Union Street, Peabody, Massachusetts.

Kenneth E. Garverick, Hunting Ridge Road, Newtown, Connecticut.

Leon Gold, 229 Park Avenue, North Caldwell, New Jersey.

A. W. Hopton, 4865 Creek Road, Lewiston, New York.

Edward F. Kelly, 1102 Cleven Avenue, Mt. Prospect, Illinois.

Robert H. Linnell, Scott Research Institute, Box 66, Perkasie, Pennsylvania.

George A. Lukas, 4 West Labonte Avenue, Saco, Maine.

Guy H. Moberg, 1011 College Avenue, Red Wing, Minnesota.

Kurt Moses, General Split Corporation, 730 W. Virginia Street, Milwaukee, Wisconsin.

Martin D. Singer, c/o Drueding Brothers Company, Wilson Hwy., Goldsboro, North Carolina.
Warner L. Smith, R. J. Widen Company, 1 Ashton Avenue, North Adams, Massachusetts.
Frederic A. Soderberg, F. C. Huyck Company, Washington Street, Rensselaer, New York.
Gilbert Thiessen, Research Department, Koppers Company, Inc., Box 128, Monroeville, Pennsylvania.
Dorothy B. Wells, Parwel Manufacturing Corporation, 34-38 West 10th Avenue, Gloversville, New York.
Robert Wright, 8446 89th Street, Woodhaven 21, New York.

ABSTRACTS

Influence of Styrene–Maleic Anhydride Copolymers on Tanning Action of Aluminum Salts. I. P. Strakhov and I. A. Gushchina. *Kozhevenno-Obuvnaya Prom.*, **3,** No. 4, 24–27 (1961).—Pelts tanned with 29% basic $Al_2(SO_4)_3$ at pH 4.2 produced leather with T_s 73°C., containing 10.8% Al_2O_3 before washing but only 1.8% after washing. Pelt that was pretanned with 0.5% and 1.0% solutions of a water-soluble styrene–maleic anhydride copolymer bound 66.0% and 73.6% respectively of the amounts of copolymer given, and pelt that was retanned with the same solutions bound 81.9% and 82.3% respectively of the copolymer. The Al_2O_3 contents of leathers pretanned with the copolymer were 8.07% and 7.65% before washing and 2.95% and 2.98% after washing. For leathers retanned with the copolymer the Al_2O_3 contents were 6.85% and 6.96% before, and 5.00% and 3.94% after, washing. The improved tannage was also shown by increase in T_s to 78°–79°C. for copolymer pretannage and to 78°C. for copolymer retannage. Water vapor permeability was unaffected by the copolymer treatments, but liquid water permeability was lowered from 15.0 ml. per sq. cm. for tannage with Al_2O_3 only to 1.6 and 2.2 ml. for copolymer pretannage and 1.6 and 2.25 ml. per sq. cm. for copolymer retannage. The copolymer retannage gave better leather than the pretannage. L.M.

Rapid Tanning of Heavy Leather. Anon. *Kozhevenno-Obuvnaya Prom.*, **3,** No. 4, 28 (1961).—Chromed pelt containing 1.5% Cr_2O_3 with surface pH 4.4–4.5 is drummed with 10–15% water at 40°–45°C. in winter or 27°–30°C. in summer, and 2% sulfated fish oil is added. After 15–20 min. vegetable tanning extract at 10.0°–18.5°Bé, adjusted to pH 5.6–6.0 by adding Na_2SO_3, is added, and drumming is continued 24 hr. Starting temperature is 26°–27°C., and final temperature is 35°–36°C. Tannin absorption is 90% to 93% complete—80% to 85% in the first 4 hr. The leather is softer than usual. L.M.

New Type of Heavy Upper Leather. F. V. Mironin. *Kozhevenno-Obuvnaya Prom.*, **3,** No. 4, 29–30 (1961).—Steerhides are soaked in a drum for 6–8 hr. at 27°–30°C. in a solution containing 0.2–0.4 g. Na_2S per l. and limed 2 days at the same temperature in liquor containing 10–12 g. CaO and 0.8–0.9 g. Na_2S per l., followed by 12–24 hr. in liquor containing 10–12 g. CaO and 2–4 g. Na_2S per l. The hides are fixed on frames in the drum. After deliming and bating, the hides are pickled normally and tanned in pickle with 1.5% Cr_2O_3 to a minimum T_s of 95°C. Retannage is done with 5–6% pure tannin (20% vegetable and 80% syntan) for 10 hr., starting at 25°–27°C. and finishing at 34°–36°C. After tanning 6 hr., there is added 3–5% of a mixture of 60% sulfated and 40% unsulfated fish oil with 0.1% nonionic emulsifier (an alkyl phenol–ethylene oxide condensate). The first finish (a casein-albumin-acrylic emulsion mixture) is applied to wet dyed leather on the frames, and the leather is dried on the frames. The dried leather gets a casein-albumin-sulfated castor oil-wax finish. Further finishing is normal. L.M.

Structure of Collagen. G. Ramachandran and V. Sasisekharan. *Nature*, **191,** 1004–5 (1961).—The triple helical structure for collagen with two systematic hydrogen bonds for every three residues is advocated on the basis of reexamination of the experimental data. The parameters of the minor helix of the collagen structure have been redetermined. These gave a value of 2.95 Å for the residue height and 3.28 for the number of residues per turn. The twist for three residues in the triple helical structure should be 30° on this basis. Where the sequence gly-pro-hydropro occurs, two bonds cannot occur systematically, and the above structure can be slightly modified locally. The calculated Fourier transform of the new structure is in good agreement with observation. C.L.D.

Structure of Feather Keratin. W. Astbury and E. Beighton. *Nature*, **191,** 171–73 (1961).—A structure for feather keratin based on the Bear and Rugo scheme of corpuscular units is proposed, in which it is assumed that 32-residue loop-corpuscles occur. C.L.D.

Crystallization in Wool Keratin. A. Skertchly. *Nature*, **191,** 138–41 (1961).—Rapid-scanning X-ray diffractometry was used to study the sequence of phases involved in the α-β transformation and the factors involved in crystallization in wool keratin. The structure of keratin is discussed on the basis of the results. C.L.D.

Supercontraction of Sound and Weathered Keratin Fibers. O. Swanepoel. *Textile Research J.*, **31,** 618–24 (1961).—Studies on the supercontraction of normal and weathered wool fibers led to the conclusion that the second stage of supercontraction results from the exposure of sterically protected hydrogen bonds. This can occur through disulfide exchange in the highly cross-linked zones of the microfibrils. Some of the cystine cross links are stabilized by weathering, so that disulfide exchange is inhibited, and hence much less contraction occurs. C.L.D.

Demonstration of Nucleases on Mammalian Skin Surface and in Saline Extracts of Hair. J. Tabachnick and R. Freed. *Nature*, **191,** 921–22 (1961).—Deoxyribonuclease and ribonuclease activities were found in saline washings derived from normal skin surfaces and clipped hair of the guinea pig, rat, and rabbit. No nuclease activity was detected on human skin.
C.L.D.

Isolation of Peptides Containing Hydroxyproline from Animal Tissues. V. Kobrle and M. Chvapil. *Nature*, **191,** 909–10 (1961).—Ultrafiltrates were prepared from homogenates of pig embryo skin. Peptide hydroxyproline formed 20–30% of the total ultrafiltrable hydroxyproline. Four peptides that contained hydroxyproline were identified by paper chromatography; these contained from 4 to 9 amino acids. Glycine, glutamic acid, proline, and hydroxyproline were found in all the peptides. It is suggested that these peptides represent precursors of collagen protein. C.L.D.

Structure of Frizzle Mutant Feather Keratin. S. Krimm. *J. Mol. Biol.*, **2,** 247–49 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 226 (1961).—The X-ray diffraction patterns of normal and homozygous feather keratins are distinctly different, while that of heterozygous keratin is roughly intermediate between the other two. The mutant keratin shows a much higher proportion of disordered material, and the crystalline component is less well oriented than in normal keratin. The mutation is probably correlated with a change in the amino acid composition of the polypeptide chains. By a solubilization method, a disordered β-keratin can be removed from feathers; this comprises 35% of normal, 50% of heterozygous, and 75% of homozygous feather.
C.L.D.

A Generalized Theory for Combination of Wool Keratin with Acid or Alkali. L. Peters. *J. Textile Inst.*, **51,** T1290–T1301 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 225 (1961).—A generalized Donnan theory, assuming ions to be adsorbed at sites, is developed to describe the titration curve of an insoluble protein that possesses unequal numbers of carboxyl and amino groups. Equations derived apply to combination with acid or alkali and include a treatment of the isoelectric point. From the constancy of the isoelectric pH of keratin it is concluded that K^+ and Cl^- do not combine with keratin.
C.L.D.

Nuclear Magnetic Resonance of Water Sorbed in Fibrous Materials. T. Shaw, R. Elsken, and R. Lundin. *J. Textile Inst.*, **51,** T562–T572 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 225 (1961).—The sorption of water in wool fibers and cortical cells was studied by nuclear magnetic resonance; proton resonance line shapes and relaxation times have been determined as functions of moisture content. It is suggested that water is bound in clusters to the sorbent and that surface migration is the dominant mode of magnetic relaxation.
C.L.D.

Effect of Chemical Modifications on Physical Properties of Wool: a Model of the Wool Fiber. W. Crewther and L. Dowling. *J. Textile Inst.*, **51,** T775–T791 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 225 (1961).—Conversion of disulfide bonds to S-methyl groups accelerates supercontraction in LiBr solutions. Evidence is presented that the rate of supercontraction is partly determined by interchange reactions between thiol and disulfide groups and that inhibition of supercontraction in the presence of free bromine is due to oxidation of thiol groups. It is concluded that contractile structures are not cross-linked by disulfide bonds but are embedded in material containing inter- and intramolecular disulfide bonds (the matrix), the rate of plastic deformation of which is affected by thiol interchange with disulfide bonds. Nitration, iodination, mild oxidative treatments, and acids and alkalies accelerate the first stage of supercontraction in 6*M* LiBr at pH 6, but they retard the second stage. This retardation does not occur in 4*M* LiBr-*N* HCl, suggesting that ionic interactions are responsible for retardation. The results are explained in terms of a model assigning low-S proteins to microfibrils and high-S protein to the intermicrofibrillar matrix. C.L.D.

Setting Properties of Keratin Fibers in Relation to Structure. J. Stoves. *J. Textile Inst.*, **51,** T603–T612 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 225 (1961).—When set at zero extension in borax solution, fibers from some animals do not contract in boiling 5% metabisulfite solution, while fibers from others contract. The results are discussed in terms of hydrogen bonds and other types of linkages. C.L.D.

Mechanical Properties of Set Wool Fibers and the Structure of Keratin. M. Feughelman. *J. Textile Inst.*, **51,** T589–T602 (1960); abstr. in *J. Soc. Dyers Colourists*, **77,** 225 (1961).—Load-extension curves in water at 20°C. of wool fibers that had been strained to varying extents in boiling water and released in water at various temperatures for one hour show considerable modifications of the initial portion of the curve for untreated fibers. The degree of modification depends on the setting strain, the time for which the fiber was held at this strain, and the temperature at which it was released after setting. The modifications are explained in terms of a series zone model for keratin. C.L.D.

Research of the Eastern German Leather Institute on Aromatic Syntans. G. Reich. *Kožařství*, **11,** 68–70 (1961).—A review of work previously published by Stather, Reich, etc., in *Ges. Abhandl. Deut. Lederinst. Freiberg/Sa.* Some new material is included. A number of definite condensation products of sulfonated naphthols and other phenolic substances have been identified and determined in syntans by splitting the compounds at the methylene bridges and determining the resulting azo dyes by chromatography. Because of the importance of sulfones in syntan manufacture, the usefulness of 4,4′-dihydroxydiphenyl sulfone substituted by halogens, nitroamino, and carboxyl groups has been studied. The kinetics of the reaction of HCHO with sulfones has also been studied as well as a series of methylene compounds that are intermediate in syntan formation. Interesting results have been obtained with dispersion syntans, i.e., unsulfonated condensation products of dihydroxy phenols, e.g.,

Difen, that are insoluble in water but are finely dispersed in the drum by vegetable tanning materials, or even by the motion of the drum alone, and are well absorbed by hide. Their leather-forming capacity is excellent, and they can replace vegetable tannins completely. This is the most important goal of syntan research. Commercial production of dispersion syntans has been started. Some components of Difen produce dark spots on leather, but this is being overcome. Uses of syntans for treating polyamide fibers, for oil well drilling, and for removing boiler scale in locomotives are being studied. L.M.

Molding of Leather in Drying Room. A. Orlita. *Kožařství*, **11,** 51–52 (1961).—Growth of most molds, e.g., *Penicilia*, is favored by prolonged drying at low temperature with slow air movement. A number of species forming colored spots on Cr leather were identified, including one (*Peacilomyces variota*) that thrives at 50°C. L.M.

Mechanization of Tanneries in Eastern Germany. M. Merx. *Kožařství*, **11,** 71–73 (1961).—The following new equipment is described: tilting paddle wheels with false bottoms, for rapid removal of liquid or transfer of skins from a higher to a lower paddle; feed-through machine for removing subcutaneous fat from pigskins and for tearing out bristles; shaving machines of 80–120 cm. working width; 170-cm. staking machines. Continuous production lines for wet operations consist of elongated pits, with slow transport between pits to permit drainage by dripping. Acceleration of many operations by use of ultrasonic waves is proposed. L.M.

Tannery Waste Water Treatment in Eastern Germany. M. Merz. *Kožařství*, **11,** 75–76 (1961).—The optimum sedimentation time is 25–30 min. Soluble material averages 10–15 g. per l. but often is 5–7 times higher. Fat must be removed from the waste water because of the high proportion of pigskins worked in eastern Germany. The sedimentation lagoons normally work 14 days, after which sludge is pumped away. Dorr thickeners are preferred. Biological final purification in filter towers 10 m. high is being tested. L.M.

Use of Polymers in the Study of Chrome Tannage. I. P. Strakhov. *Kožařství*, **11,** 10–15 (1961).—Combination of Cr with collagen has been studied by using model substances. An ε-caprolactam polyamide binds 2.93 meq. of acid or 0.88 meq. of base per 100 g., compared to 88–94 meq. acid or 46–78 meq. base for collagen. Thus ε-caprolactam polyamide contains very few NH_2 and COOH groups and binds no cationic or anionic Cr complexes, not even 55% basic complexes of molecular weight 2000. Silk fibroin binds 1.34–1.62% Cr_2O_3 compared to 6.45–12.00% by collagen. The work of Gustavson on Cr tannage of Igamid 6A was not confirmed. Igamid 6A contains modified -CO-NH- groups and contains 0.52% of amino N, compared to 0.11% in ε-caprolactam polyamide and 3.15% in collagen. Igamid 6A binds 6.78 meq. of acid and 2.40 meq. base, which also indicates that Igamid 6A has been modified in comparison with the ε-caprolactam polyamide (USSR Kapron) used in these and preceding experiments of the author. Tannage of Igamid 6A with cationic $CrCl_3$, at 33% and 56% basicities, gave fixations of 0.17 and

0.72% Cr_2O_3, while Gustavson reported fixations only from anionic and non-ionic Cr solutions. Fixation of Cr depends on the state of modification of the polyamide; it is not fixed by peptide groups but only on NH_2 or COOH groups of Igamid 6A or any other modified polyamide. Modification of polyamide also influences fixation of vegetable tannins by H-bonding. Kapron was modified by treatment with phenol. Unmodified and modified Kapron absorbed 1.86% and 14.20% organic matter respectively, including 1.15% and 12.35% respectively of "bound" tannin, and 0.37% and 7.67% respectively of "fixed" tannin. Phenol-modified Kapron also binds Cr. Previous experiments on fixation of Cr by ion exchangers have been confirmed and extended. From 33% basic $CrCl_3$ (cationic) the cation exchanger Wofatit R fixes 8.2 meq. Cr per 10 g., and the anionic exchanger Dualit A-2 fixes 22.8 meq Rate of travel through the columns was 100 ml. per min. Cr adsorbed by a Kationit K14 column was not eluted by water. HCl (2*N*) removed 21–26% of the sorbed Cr from a column prepared with *N* HCl, and *N* NaCl-2*N* oxalic acid removed 70.5% of the sorbed Cr. The remaining Cr probably is bound by COOH groups. **L.M.**

Gas Chromatography in the Leather Industry. Z. Hrabal. *Kožařství*, **11,** 3–5 (1961).—The applications of gas chromatography to control of ethylene absorption in the manufacture of ethylene chlorohydrin for butyl acrylate production and analysis of shoe cement solvents are described. **L.M.**

New Machinery and Equipment in USSR Tanneries. M. Spicka. *Kožařství*, **11,** 18–20 (1961).—A lattice drum with a capacity of 5600–5800 kg. fresh steerhides suspended on 12 frames (USSR patent 117233) is used for soaking and liming. The hides are washed 1–2 hr., soaked 22 hr. in fresh water with intermittent drumming, and limed 48 hr., with drumming for the 1st 5–6 hr. and 5–10 min. per hr. thereafter, in 500% water, 5.5% CaO, and 0.35% Na_2S (60%) at 25°–28°C. Quality of pelt is good, and hair is not damaged. Other new machines are: (1) combined unhairing and scudding; (2) sole leather scouring and filling; (3) a feed-through, 1.8-m.-wide sole leather setting; (4) oiling off; (5) a feed-through, 1.8-m.-wide sole leather calender; (6) electronic thickness and measuring machine for sole leather; (7) a Ukrainian machine that sorts sole leather into 3 thickness and 4 quality grades, packs 20 bends in a bundle, and marks the quality on electric contact; (8) 3 types of sole leather drying and humidifying tunnels. **L.M.**

Final Finish of Glove Leather. P. Němecek. *Kožařství*, **11,** 47–49 (1961).—High-quality glove leather is dyed and finished by plushing. Lower quality is stretched on frames and sprayed with BKM 82R dispersion (better than Corialgrund O) and casein solution. Modified casein or Luron binder finishes are not rubfast. **L.M.**

The Tannins of Spruce Bark. XV. Total Analysis of Polyhydroxyphenols of Spruce Bast. H. Endres. *Das Leder*, **12,** 152–57 (1961); (see *JALCA*, **55,** 356).—Extraction of spruce bast with alcohol after thorough extraction with ethyl acetate yielded 20% of material that was absorbed by hide powder and that had almost the same composition as the ethyl acetate

extract. The bark residue when heated with water yielded a dark brown material which consisted mainly of condensation products that could not be identified. Yields of material, on the dry bark basis, and characteristics of the extracts from successive extractions with ethyl acetate, alcohol, and water resp. were as follows: yields, 12.6%, 12.7%, and 17.0%; purities, 80.1, 39.1, and 57.9; tan values, 60, 69, and 54; combining values, 7, 42, and 37; and tanning action on hide, poor, good, and excellent. An efficient solvent for extracting bark was a 1:1 mixture of alcohol and water at 50°–60°C. It removed from fresh spruce bast (with exclusion of oxygen) 85% of the compounds shown by the Official Method to be extractable from bast and absorbable by hide powder. This bright yellow extract had a purity of 52%, which was raised to 75–80% by leaching with chloroform and then to 90% by purification on a polyamide column. From the spent bast, after the alcohol-water leach, 20% of material could be extracted with boiling water, but this material was not a polyhydroxyphenol. No essential differences were noted between chromatograms of alcohol-water extracts and ethyl acetate extracts; also there were almost no differences between column chromatographs on polyamide powder of the two extracts or between chromatograms of the aglycon mixtures after enzymatic removal of sugars. The following phenolic compounds, with yields based on phenolic fraction and on dry bast weight resp., were isolated: piceatannol mono- and diglucosides, 50–55%, 7–8%; dihydropiceatannol monoglucoside, 10–15%, 1.5–2%; piceatannol, 5–10%, 0.5–1.5%; trihydroxytetralin monoglucoside, 2–3%, 0.3–0.45%; dihydropiceatannol, 2%, 0.3%; quercetin and its monoglucoside, 10–12%, 1.5–1.8%; catechin, 2–5%, 0.3–0.7%; and kaempferol-3-glucoside.

I.D.C.

The Tannin of *Acacia Saligna*. H. El Sissi and A. El Sherbieni. *Das Leder*, **12**, 150–52 (1961).—*Acacia saligna*, a native of Australia and known there as Port Jackson willow, has been reported to contain 15–20% tannin. The bark of 5-year-old trees grown in Egypt contained about 5% tannin (purity 47.5%), and the leaves also contained 5% tannin (purity 20.0%). The tannin was of the condensed type, with a small amount of the hydrolyzable type. Leaf material, after removal of chlorophyll by extraction with chloroform, was extracted with four solvents in succession with the following results: ether, 1.13% of green extract; ethyl acetate, 21.7% of yellow-brown extract containing 0.54% tannin; ethanol, 10.14% of light brown extract, 1.94% tannin; and water, 23.64% of dark brown extract with 6.21% tannin. Total tannin extracted was therefore 8.7%. Flavonoids were found in all fractions except the water extract. Sucrose, glucose, fructose, and raffinose were detected as free sugars in the various extracts, and rhamnose, glucose, and fructose as bound sugars. Chromatograms showed the following total number of spots and spots colored by phenol reagents: ethyl acetate extract, 10 and 9 resp.; alcohol, 18 and 13; and water, 17 and 16.

I.D.C.

The Question of Costs for Leather Finishing. J. Wagner. *Leder Kurier*, **5**, 79–84 (1961).—The costs of the various tanning stages for producing box-side leather, as proportion of total cost, are about as follows: raw hides, 68%; beamhouse operations, 2%; tanning, 5%; dyeing and fatliquoring, 4%; drying, 8%; and finishing, 13%. Material, power, and labor costs for the different steps in finishing leathers of different colors are given; red leather

cost most, and black leather least, to finish. A modern, although expensive, machine may give greater production and therefore less cost per square foot of leather than an older machine. I.D.C.

Autoxidation of Vebetable Oils in the Leather Industry. G. Vágó, J. Réti, and P. Varga. *Das Leder*, **12**, 144–50 (1961); from *Acta Chimica Hungarica*, **20**, 367–79 (1959).—Sunflower oil, used in fatliquoring upper leather in Hungary, may cause leather damage through oxidation and heating; however, not over 10% of the leather in factories during the hottest weather showed signs of heating. Heating depends on the unsaturation, peroxide number, and iron content of the oil, and on the possibility of heat storage in the leather. In autoxidation, oxygen of the air adds to a double bond to form a hydroperoxide which may then react with another double bond. Tendency to autoxidation was measured in the Mackey apparatus. Iron catalyzed decomposition of the hydroperoxide, but chromium, aluminum, and copper had only slight effects. Antioxidants were effective in reducing heating; the best were hydroquinone, propyl gallate, and 2-naphthol. Ineffective were hydroxyphenyl stearic acid and brown coal tar fractions rich in diphenols. Addition of complexing compounds, such as Complexon III or tartrates, which mask iron were quite effective. Also effective were thiocarbamide, thiosulfate, and especially sodium tetrasulfide. Dilution with spindle oil had no effect, but chlorinated gas oil reduced oxidation if a rather large amount was added. Partial sulfonation of the oil to reduce its unsaturation was quite effective. Epoxy compounds which formed during oxidation had a definite tanning action. I.D.C.

PATENTS

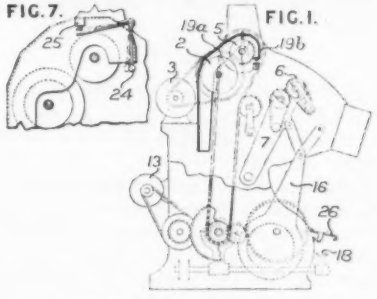
Waterproofing Leather. Brit. Pat. 867,193. Chemical Materials Pty. Ltd. Filed Dec. 17, 1958.—Leather is waterproofed by preheating followed by immersion in a molten composition consisting of liquid polyisobutylene, the monostearate of sorbitol anhydrides, a low-melting point paraffin wax and a high-melting point wax such as microcrystalline wax or a paraffin wax, the leather then being withdrawn, allowed to drain, transferred to a hot air chamber, placed in a scour solution which is subsequently washed off with cold water and the leather then being allowed to dry.

Waterproofing Textiles, Paper, and Leather. Brit. Pat. 868,080. Farbwerke Hoechst A.G. Filed Nov. 1, 1957.—Hardenable condensation products comprising methylol or substituted methylol derivatives of substances prepared by treating polyamines with substances which introduce urea groups into them and with long-chain substances containing groups reactive with amino and carbonamide groups (*see* Group IV (a)) are used for impregnating paper, textiles or leather to render them water-repellent. The products may be used as aqueous solutions or emulsions and in conjunction with aminoplasts or their precondensation constituents, polyvinyl compounds, or paraffin or other waxes. In Example 1 (*d*) a paste obtained by treating diethylene triamine with urea, stearyl chloride and then formalin was stirred with a solution of paraffin

wax in chlorobenzene, diluted with water and aluminium sulphate was added as a catalyst. Cotton poplin was impregnated with the mixture, dried and heated to give it water-repellent properties. (2) A staple film fabric was similarly rendered water-repellent by treatment with an aqueous solution containing hexamethylol melamine, ammonium nitrate as a catalyst, and a paste obtained by reacting ethylene diamine with urea, octadecyl isocyanate and formalin.

Leather Replacement. U. S. Pat. 2,994,630. R. O. Osborn, Snyder, N. Y., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware. Filed May 17, 1957.—1. A water vapor permeable, scuff-resistant, flexible leather-substitute sheet material comprising a base stratum containing predominantly a mat of non-woven organic fibers bound together by an extensible polymeric binder and a surface stratum of non-woven glass fibers bound together by an extensible polymeric binder, said sheet having a network of pores substantially contiguous with fibers throughout the thickness of the sheet.

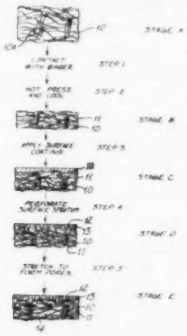
Leather-working Machines. Brit. Pat. 866,682. Mercier Freres. Filed Aug. 7, 1958.—In a machine, such as a tannery machine, having moving parts, some of which are protected by a cover while others are exposed, the cover, or a part thereof, is movably mounted and associated with an electric switch controlling



the exposed moving parts so that any shock or force exerted on the cover (e.g. by an operator who has lost his balance) causes the stopping of the exposed parts. The tannery machine shown comprises a bladed roller 2 which is belt-driven by a motor 3, a roller 5 which is chain-driven by a motor 13, and one or more conveying rollers 6 on an arm 7 which is oscillated between open and closed positions by an eccentric mechanism 16. The mechanism 16 is driven by the motor 13 through a coupling controlled by a pedal 18. When the arm 7 is in the closed position the conveying rollers 6 lie adjacent to and are driven by a gear fast with the roller 5; alternatively the conveying rollers may be driven by a belt which is tensioned only when the arm 7 is closed. The upper part of the machine is protected by a fixed cover part 19*a* to which is hinged, e.g. by a flexible plate, a movable cover part 19*b* associated with a microswitch so that any displacement of the part 19*b* stops the motor 13 and applies a brake associated therewith. In a modification the whole cover is in one piece and is movably carried by swinging links, Fig. 5 (not shown). In

addition to the movable cover or cover part, the machine may be provided with switch-actuating trip-bars such as 24, Fig. 7, in front of dangerous spaces, the bar co-operating with a microswitch 25. The pedal 18 also has a pivoted guard 26, or a trip-bar, co-operating with a microswitch. All the microswitches are connected in series with a coil of a contactor circuit-breaker for the motor 13, the circuit, Fig. 10 (not shown), including remote stopping and starting switches, a local starting button and a thermal relay. Specification 741,916 is referred to.

Leather Substitute. U. S. Pat. 2,994,617. J. S. Proctor, Grand Island, N. Y. assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware. Filed Nov. 5, 1956.—



1. A process for making a water vapor-permeable, scuff-resistant, flexible sheet material suitable for use as a leather replacement which comprises bringing together a non-woven mat of polyhexamethylene adipamide fibers and a polyvinyl chloride plastisol in a polyvinyl chloride: fiber weight ratio of from about 30:70 to 70:30, forming a compacted base stratum in which the said mat of fibers is substantially embedded in the fibers thereof are bonded by the polyvinyl chloride by heating the resulting mixture at 150°C.°200–C. under pressure of 50–1500 pounds per square inch followed by cooling under pressure, coating one surface of the base stratum with polyvinyl chloride to obtain an adherent polyvinyl chloride surface stratum 1–20 mils thick, needle punching thru the surface stratum and part way into the base stratum with needles of 1–10 mils diameter to provide from 300–30,000 perforations per sq. in. in the surface stratum, and stretching the surface coated base stratum from 10–50% in at least one direction to cause fibers to break away from polyvinyl chloride in said base stratum and form a network of interconnecting pores.

Protein Fiber and Method. U. S. Pat. 2,992,933. M. M. Besso, Bethlehem, Pa., A. F. Diorio, Washington, D. C., and W. L. Hochner, Jamaica, N. Y., assignors to National Lead Company, New York, N. Y., a corporation of New Jersey. Original application Mar. 25, 1957. Divided and this application Mar. 6, 1958.—1. A textile fiber consisting essentially of a regenerated protein and an alkyl aryl sulfonate detergent, in a ratio between about 85 parts of protein to about 15 parts of sulfonate and about 89 parts of protein to about 11 parts of sulfonate.

2. A fiber, according to claim 1, wherein said regenerated protein is a linseed protein.

Tanning Leather. Brit. Pat. 863,505. Farben-Fabriken Bayer A.G. Filed July 9, 1959.—A synthetic tanning agent is produced by condensing, in the presence of an acid catalyst, an aromatic hydrocarbon having condensed benzene nuclei, formaldehyde or a substance yielding formaldehyde under the reaction conditions, and an aromatic carboxylic acid containing at least one hydroxyl group. Specified aromatic hydrocarbons are naphthalene, anthracene and phenanthrene, and several alkyl and alkoxy naphthalenes are also listed. Salicylic acid is particularly suitable as the aromatic hydroxy acid, but 4-hydroxy benzoic acid and the cresotic acids are also mentioned. The resinous products can be brought into aqueous solution as their alkali metal, ammonium or amine salts, and can be precipitated from aqueous solution by salts of chromium, aluminium, iron or zirconium or by acids. In an example, a shaved full chrome-tanned cowhide, which in the cut of the leather showed a *p*H of 4.3 to 4.5, is drummed in an aqueous solution of a resinous condensation product obtained, in the presence of aqueous hydrochloride acid, from salicylic acid, naphthalene and an aqueous solution of formaldehyde, and afterwards is fat liquored and finished in the usual manner to give a full leather with a firm, tight grain.

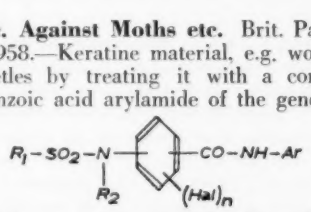
Coated Leather. Brit. Pat. 863,771. Soc. Des Usines Chimiques Rhone-Poulenc. Filed May 1, 1959.—A flexible glossy coating is formed on leather by applying thereto a composition comprising, by weight: (a) 4 to 30% of a methylphenylsiloxane resin having a ratio of methyl and phenyl radicals to silicon of 1.3 to 1.6, a ratio of phenyl radicals to silicon of 0.4 to 0.7, and from 1 to 5% of Si-bonded OH groups, and having, in 70% by weight solution in toluene, a viscosity below 120 cs. at 20°C.; (b) 1 to 20% of a wholly organic film-forming resin which dries to a glossy film in ambient air; and (c) 50 to 95% of a volatile solvent for the resins (*see* Group IV (a)). Resins (b) specified are polyvinylacetals having a softening point between 50° and 65°C., e.g. polyvinyl butyrals and hexanols having a degree of acetalization of from 95 to 100%, and solid acrylic and methacrylic polymers having a softening point between 50° and 80°C. Solvents specified are ethyl and butyl acetates, xylene, isopropanol, acetone, methylethylketone and any mixture thereof. The compositions may be applied as by pad, brush or domestic sprayer, or, where the solutions are compatible with propellants such as butane or chlorofluoromethanes, as aerosols. Perfumes, dyes and pigments, e.g. bronze powder, may also be added. Examples are given.

Tanning Leather. Brit. Pat. 864,079. Farbenfabriken Bayer A.G. Filed Nov. 26, 1958.—Synthetic tanning agents, which are practically free from ash and have a purity number greater than 90, are prepared by reacting a phenol or a polyphenol with a molar excess of formaldehyde in the presence of a small amount of an alkali metal hydroxide, neutralizing the mixture and, after separation of the low molecular weight salt-containing resin, further reacting it with ammonium bisulphite. Phenols and polyphenols specified are phenol itself, *o*-, *m*- and *p*-cresols, *o*-, *m*- and *p*-chlorophenols; dihydroxydiphenylmethane, dihydroxydiphenyl-dimethylmethane, dihydroxydiphenylsulphone and the cor-

responding dihydroxydiphenyl compounds obtained from the other above-specified phenols; empyreumatic oil; and low molecular weight novolacs. The ammonium bisulphite is preferably formed during the reaction by first adding ammonia and then introducing gaseous sulphur dioxide. The tanning agents can be used not only for the manufacture of white leather but also as pre-tannins, re-tannins and exchange tannins; they are especially useful for continuous use in the pit systems. In Example 2, a cow-hide, limed, split to 3 mm., delimed and mordanted in the usual manner, is drum tanned with a tannin mixture consisting of 250% water, 7% pure tannin Quebracho sulph., 7% pure tannin Mimosa sulph. and 7% pure tannin prepared by reacting ammonium bisulphite with a low molecular weight novolac which has been further reacted with formaldehyde in the presence of sodium hydroxide; the leather is then fatliquored and finished in the usual manner. Another example describes the pre-tanning of a cow-hide with a tanning agent of the invention followed by treatment with vegetable tanning agents. Other examples describe the treatment of goat-hides and cow-necks.

Tanning Leather. Brit. Pat. 866,411. Nopco Chemical Co. Filed Oct. 14, 1958.—Cationic aminoplasts prepared from dicyandiamide, urea and formaldehyde (*see* Group IV (a)), are useful for tanning leather. They may be used alone, or as a pre-treatment or after-treatment in vegetable tanning, or for filling chrome-tanned hides either alone or as a topping after pretreatment with anionic compounds, or in conjunction with an anionic compound for fixing a shrunken grain effect. Examples describe in detail the treatment of bated calf skins with specific resins according to the invention, both alone and in conjunction with anionic tanning-agents. They also describe the use of the same resins for after-treatment of chrome-tanned hides.

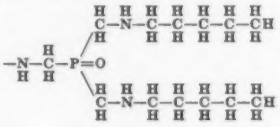
Proofing Wool etc. Against Moths etc. Brit. Pat. 865,735. Geigy A.G., J. R. Filed Dec. 18, 1958.—Keratine material, e.g. wool and fur, is protected against moths and beetles by treating it with a composition comprising a N-sulphonated aminobenzoic acid arylamide of the general formula



dissolved or suspended in an inert solvent, if desired in the presence of an emulsifying agent. In the above formula Ar represents a phenyl, phenoxyphenyl, phenylmercaptophenyl radical, which radical is substituted by at least one halogen atom and/or trifluoromethyl group, R_1 represents a halogen-substituted lower alkyl group or a phenyl or phenylalkyl group substituted in the nucleus by halogen and/or trifluoromethyl, R_2 represents hydrogen or a lower alkyl radical, Hal represents chlorine or bromine, and n is a whole number from 0 to 4, and wherein the total number of halogen and trifluoromethyl substituents present on the different aromatic rings of the molecule is greater than 2 and preferably at least 4. Two processes for producing these compounds are described (*see* Group IV (b)). When R_2 is a hydrogen atom, the compounds form alkali metal salts of good water-solubility. Suitable organic solvents for the compounds are the following: propylene glycol, dimethyl formamide, and the monomethyl and monoethyl esters of ethylene glycol. Specified emulsifying agents are:

sulphonated castor oil, sulphite waste liquor, and fatty acid sulphonates. Examples 4, 5 and 6 describe suitable aqueous liquors, each containing a specified active compound, for the treatment of wool.

THPO Tanned Leather. U. S. Pat. 2,993,744. L. G. Picklesimer, Dayton, Ohio, assignor to the United States of America as represented by the Secretary of the Air Force. Filed Feb. 18, 1959.—1. Leather comprising collagen with its amino group of the structure:



Hide Soaking Bactericidal Composition and Process for Using the Same. U. S. Pat. 2,998,293. H. Damm, Duesseldorf-Benrath, and W. Fischer, Duesseldorf, Germany, assignors to Boehme Fettchemie G.m.b.H., Duesseldorf, Germany. Filed Sept. 10, 1956.—2. An aqueous soaking composition having a pH of 7.5 to 8.5 for the soaking of furs and hides after skinning to prevent the growth of proteolytic bacteria causing sliminess and odors in the solution and on the hides so-treated, said aqueous composition containing as the essential antibacterial substance therein at least about 0.0005% and not more than about 0.01% by weight of said solution of actinomycin A and B with another antibiotic in a concentration of at least about 0.0005% and not more than 0.001%, of said solution, said other antibiotic selected from the group consisting of chlorotetracycline, chloramphenicol, penicillin and mixtures thereof.

Process for Improving Chrome Tanned Leather. U. S. Pat. 2,998,294. C. T. Locke, Plymouth, Wis., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware. Filed Aug. 7, 1959.—1. The process for improving chrome tanned leather which comprises impregnating fully chrome tanned leather at a temperature of from about 80°F. to about 120°F. with an aqueous solution of a water-soluble inorganic acidic salt of a metal or the group consisting of aluminum, zirconium and zinc in an amount to provide from about 0.5% to about 2.5% by weight of said salt based on the leather, then impregnating the leather at a temperature of from about 75°F. to about 135°F. with an aqueous solution of di(methoxymethyl)dimethylolurea in an amount to provide from about 1.5% to about 30% by weight of said urea based on the leather, and then impregnating the leather at a temperature of from about 80°F. to about 135°F. with an aqueous solution of a water-soluble inorganic acidic salt of a metal of the group consisting of aluminum, zirconium and zinc in an amount to provide from about 0.5% to about 10% by weight of the acidic salt based on the leather.

Tanning with Lignin Sulfonic Acid-Chromium Compound Reaction Product. U. S. Pat. 2,995,415. R. G. Banner and J. H. Pierce, Painesville, Ohio, assignors to Diamond Alkali Company, Cleveland, Ohio, a corporation of Delaware. Filed May 4, 1960.—1. In the tanning of leather the method which comprises the step of subjecting the material to be tanned to an aqueous

solution of a predominantly non-ionic, chromium-containing reaction product obtained by chemically reacting lignin sulfonic acid with a hexavalent chromium compound in an amount within the range of 25% to about 50% by weight of the lignin sulfonic acid expressed as lignin solids, to obtain a reaction product containing a major proportion of non-ionic chromium.

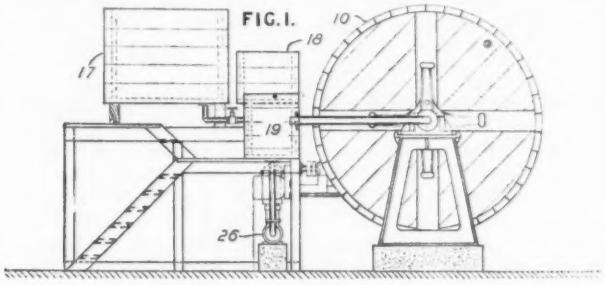
Production of Complex-Metal Tanning Agents. U. S. Pat. 2,997,363. T. Pfirrmann, Ludwigshafen (Rhine), Germany, assignor to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany. Filed Mar. 26, 1956.—1. A process for the production of tanning agents which comprises mixing together (I) one mol of a tanning salt of a complex-forming polyvalent metal, said salt being dispersible in water with an acid reaction and being selected from the group consisting of zinc, aluminum, titanium, zirconium, chromium and iron with (II) about ½ to 2 mols of an amine containing at least one hydrogen atom on one amino group, adding (III) a member of the class consisting of formaldehyde, paraformaldehyde, and polyglyoxal and condensing the product of (I), (II) and (III) in the presence of (IV) an aromatic hydroxy compound with (V) a condensation product of formaldehyde with a member of the class consisting of urea, melamine, dicyandiamide, ethyleneglycol-diurethane containing at least one hydrogen atom on one amino group and butane-diol-diurethane, in which process the amount by weight of (IV) is about ⅓ to 1½ that of (I)+(II) and the amount of (V) is about three times to ten times that of (I)+(II), calculated on the dry content of these substances.

Chrome-tanning Mixtures and Preparation of Leather Therewith. U. S. Pat. 2,997,364. E. Komarek, Leverkusen, and G. Mauthe, Opladen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany. Filed Dec. 2, 1957.—2. A process for the manufacture of leather which comprises pretanning a hide with a mixture of a trivalent chromium tanning salt and a synthetic tanning agent prepared by condensation of an unsulfonated methylolated phenol with a member of the group consisting of a sulfite and a bisulfite in the presence of a member selected from the group consisting of an alcohol, analdehyde, and a ketone under alkaline conditions.

Tanning with Tetrakis (Hydroxymethyl) Phosphonium Chloride and Phenol. U. S. Pat. 2,992,879. W. Windus, Meadowbrook, E. M. Filachione, Philadelphia, and W. F. Happich, Jenkintown, Pa., assignors to the United States of America as represented by the Secretary of Agriculture. Filed Sept. 25, 1959.—1. A process for tanning skins comprising impregnating skins with a buffered aqueous solution at pH in the range of about 4.0 to 4.5 containing tetrakis(hydromethyl)phosphonium chloride and a compound selected from the group consisting of phenols and phenol acids, and adjusting the pH of the solution during the tanning operation to a maximum pH in the range of about 8.5 to 9.5.

Liquid Circulation Systems for Treating Hides and Skins. Brit. Pat. 839,055. Ingle Ltd., W. L., and Wilson & Son Ltd., E. Filed Sept. 30, 1958.—An apparatus for the treatment of hides, skins and the like comprises a rotary

drum 10 having an axial liquid inlet and outlet, connected by external piping wherein there is interposed a circulating pump 26 and a feed means, tanks



17, 18, 19, whereby reagents may be introduced into the circulation system, 19 being a test tank into which reagents from a supply tank or tanks 17, 18 may be measured and mixed. The floor of the test tank may be below the normal liquid level of the drum whereby samples of liquid circulating through the drum may be taken without the necessity of stopping or slowing the action of the drum.

Coated Fabrics; Laminates; Leather; Paper etc. Brit. Pat. 868,333. Ciba Ltd. Filed Mar. 5, 1958.—Hides, pelts, leather, woodpulp, paper, cardboard, compressed wood, hollander pulp and coatings and dressings for textiles and paper are screened from the deleterious action of ultraviolet light by the incorporation of light-screening agents comprising hydroxyketones of the formula R_1COR_2, in which R_1 represents an ortho-hydroxy phenyl radical, which may be further substituted, and R_2 is a 1:1'-diphenyl radical bound in the 4-position to the CO group.

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ERRATA

In the September number the following errors appeared:

p. 531, the third abstract, l. 3: "**56,** 00" *vice* "**56,** 462"

p. 532, the third abstract, l. 16: "Magnetic construction" *vice* "magnetic constriction"

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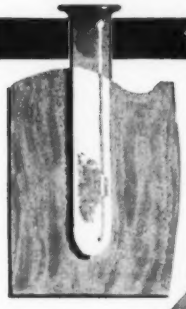

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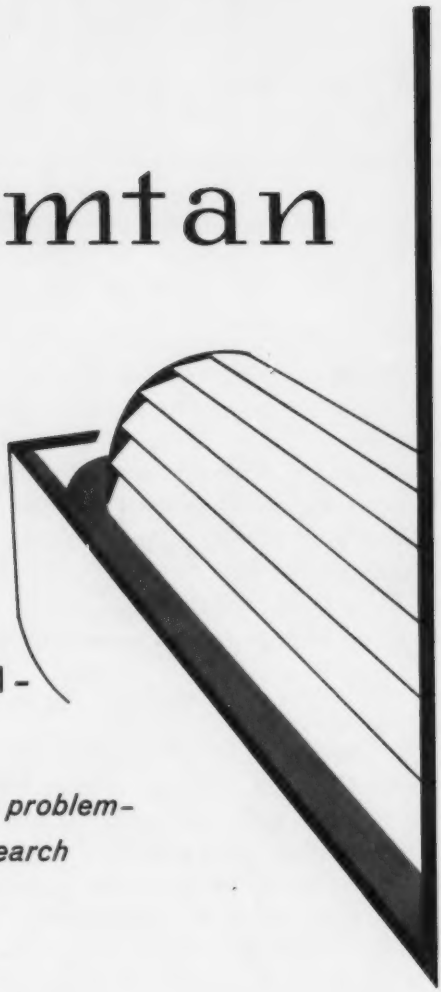

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